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THE RESULTS OF LONG-TERM STORAGE TESTS FOR COMPATIBILITIES OF SPACECRAFT MATERIALS WITH HYDRAZINE AND HYDRAZINE MIXTURES

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ANALYSES AND INSTRUMENTATION

Copy No.1.....

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ABSTRACT

The results of compatibility tests are summarized for various metallic and polymeric specimens which had been stored in sealed capsules with hydrazine, hydrazine-hydrazine nitrate, and hydrazine-UDMH at 110°F for periods of about 2 to 4 years. It was found that platinum, an aluminum alloy, and an ethylene-propylene polymer were compatible with hydrazine, and an aluminum alloy and some specially-treated titanium alloys were compatible with hydrazine-hydrazine nitrate. Only one titanium alloy was tested with hydrazine-UDMH and it was determined to be incompatible. The corrosion rates of all specimens in the amine fuels were less than 3 μ in/yr. The materials were prepared and stored in contact with the amine fuels by the Jet Propulsion Laboratory and various contractors; terminal analyses were performed by the Stanford Research Institute.

Examination of the storage tests included analyses of fuel compositions and ullage gases, microscopic study of specimen surfaces, and measurements of ullage gas pressures and volumes, specimen weights, and fuel weights. The results of the analyses are given in tabular form, supplemented by photographs of the specimens.

Compatibility ratings were established with reference to the decomposition rates (and pressures) of hydrazine control samples. It is shown that under the storage conditions imposed, hydrazine decomposition proceeds preponderantly according to the equation: $3 \text{N}_2\text{H}_4 \rightarrow 4 \text{NH}_3 + \text{N}_2$.

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I. INTRODUCTION

A portion of the program for advanced liquid propulsion systems at the Jet Propulsion Laboratory, California Institute of Technology, is concerned with the design of liquid propulsion systems which employ storable propellants such as hydrazine and nitrogen tetroxide. The systems are to be operable on command while in the space environment for more than two years. In order to select suitable materials of construction for the $\text{N}_2\text{H}_4\text{-N}_2\text{O}_4$ system, a variety of commercial alloys, refractories, and polymers have been stored with propellants in sealed capsules at 110°F for periods of time in excess of one year.

Under Contract 951581 with the Jet Propulsion Laboratory, Stanford Research Institute has undertaken to analyze a number of the stored samples and propellants (Phase 1). The results of storage tests with nitrogen tetroxide are summarized in Special Report No. 2 (951581-2), May 15, 1967. This report summarizes the results of 51 storage tests of various materials in hydrazine, mixtures of hydrazine and hydrazine nitrate, and hydrazine and UDMH.

Section II describes the preparation and storage of the samples by JPL. Section III describes the procedures used by SRI for the analysis of the hydrazine fuels, the ullage gases, and the various materials stored with the fuels.

The results of the analyses are presented in tabular form in Sections IV (hydrazine), V (hydrazine-hydrazine nitrate), and VI (hydrazine-UDMH); these Sections include also photographs of the materials after storage and a brief discussion of the results. Section VII has a discussion of the decomposition of hydrazine and its storage problems.

The Appendixes outline the JPL cleaning and passivating procedures for specimens prior to storage and the compositions of materials and alloys used in these tests.

II. PREPARATION AND STORAGE OF SAMPLES (JPL)

The storage capsules of about 75cc volume were made of Pyrex glass attached to stainless steel Bourdon-type gages by means of Kovar-to-glass seals and stainless steel Swagelok fittings; each component was Lox-cleaned prior to assembly, and the gages were calibrated to read psia. The amine fuels used in the storage tests were:

- (1) propellant-grade hydrazine
- (2) hydrazine-hydrazine nitrate mixture
- (3) 50-50 hydrazine-UDMH* mixture (Aerozine).

The specimens were generally cylindrical rods of about 1/4" diameter and about 3" long; included in the storage tests were strips of ethylene-propylene elastomer (EPR) and EPR bonded to titanium in a configuration used in flight tanks. They were cleaned and passivated according to JPL Spec No. GMZ-50521-GEN-A and introduced into the capsules, the Kovar-to-glass connection was made, and then the gage was attached with the Swagelok fittings, using thin Teflon tape as a sealer. The amine fuels were introduced into the capsules in an amount which provided two-thirds to total immersion of the specimens (see Fig. 1). Each capsule was immersed in a dry-ice/alcohol mixture, the volume over the fuel evacuated to less than 1 torr, and the final seal was made. Four capsules, containing control samples of the hydrazine-hydrazine nitrate mixture were sealed in all-glass systems (without gages); four concurrent tests were set up with gages.

The information provided SRI on the JPL storage tests is summarized in Tables 1 to 3, including weights, dimensions, and storage data; initial fuel analyses (JPL) are given in Table 4. Passivation

* UDMH, unsymmetrical dimethyl hydrazine

procedures for the specimens, listed in Tables 1 to 3 according to JPL Log numbers, are described in Appendix A of this report.

The test capsules examined in this phase of the work had been in storage at a temperature intended to be $110 \pm 5^{\circ}\text{F}$ for periods of from 1-3/4 to 4-1/2 years. During storage at the JPL Edwards Test Station, Edwards Air Force Base, the pressure reading of each capsule was recorded every few days; the pressure data are plotted in Figs. 2 to 9 for each storage test. Also indicated on the pressure plots is the terminal pressure at 75°F as measured at SRI. All storage tests, without exception, showed a gradual increase in pressure with time, and in all cases (but one) the pressure within the capsules at the end of one year's storage was in excess of the estimated vapor pressure at $110 \pm 5^{\circ}\text{F}$ for the various fuels as shown below:

<u>Fuel</u>	<u>Vapor Pressure</u>
N_2H_4	0.7-0.9 psia
$\text{N}_2\text{H}_4\text{-N}_2\text{H}_5\text{NO}_3$	0.6-0.8 psia
$\text{N}_2\text{H}_4\text{-UDMH}$	2.5-3.2 psia

Although a casual review of storage pressure readings indicate, in general, that there was a slow and fairly uniform increase of pressure with time at different rates for each test capsule, a closer examination of the data shows that for most samples a rather abrupt increase in the rate of pressure build-up occurred at some time during storage. This change occurred at different times of storage for the various tests, but at the same calendar time, i.e., during June 1966. The storage pressure readings for several tests are plotted in Fig. 10 and the plot suggests that these abrupt increases in pressure are probably caused by a change in the set-point of the storage temperature control. Subsequently, mild to steep acceleration of fuel decomposition can be observed.

At the termination of the storage tests (June 1967), the capsules were cooled and shipped to SRI packed in dry ice.

Table 1

IDENTIFICATION OF JPL STORAGE TESTS IN HYDRAZINE:
TREATMENT, DIMENSIONS, AND STORAGE DATA

JPL TEST NO.	MATERIAL	PASSIVATED ^a JPL LOG NO.	WEIGHT, g	AREA, cm ²	STORAGE TIME, yr	DEPTH OF IMMERSION	FINAL STORAGE PRESSURE AT 110°F, psia
0094	Platinum	--	0.3189	5.7	4.1	Total	20.0
0105	6061-T6 aluminum alloy + Rulon ^b coating	0088	5.9015	14.9	3.9	2/3	27.5
0107	6Al-4V titanium alloy + Apiezon-L grease coating	0093	9.3964	14.9	3.9	1/2	28.5
0108	6061-T6 aluminum alloy + Apiezon-L grease coating	0088	5.8977	14.9	3.9	2/3	17.5
0133	6061-T6 aluminum alloy, brazed joint	--	5.2111	13.4	3.9	Total	21.0
0138	Control, for 0133	--	--	--	3.9	--	25.5
0155	Ethylene-propylene co-polymer (E515-8)	0124	--	--	3.7	Total	19.0
0179	Control, for 0181	--	--	--	3.1	--	10.5
0181	Ethylene-propylene co-polymer (E515-8) + 6Al-4V titanium alloy	--	--	--	3.1	Total	38.5
0243	356-T6 aluminum alloy	--	5.7508	14.9	2.2	2/3	10.0
0244	356-T6 aluminum alloy	--	5.7221	14.9	2.2	2/3	4.5
0245	Control for 0243, 0244	--	--	--	2.2	--	9.0

^a) All samples (except 0094, 0133, and 0155) cleaned according to JPL Log No. 0087 and passivated according to listed Log Nos. See Appendix A for details.

^b) Rulon, a fluorocarbon-based spray, Connecticut Hard Rubber Co.

Table 2
IDENTIFICATION OF JPL STORAGE TESTS IN HYDRAZINE-HYDRAZINE NITRATE:
TREATMENT, DIMENSIONS, AND STORAGE DATA

JPL TEST NO.	MATERIAL	PASSIVATED ^a JPL LOG NO.	WEIGHT, g	AREA, cm ²	STORAGE TIME, yr	DEPTH OF IMMERSION	FINAL STORAGE PRESSURE AT 110°F, psia
0042	6061-T6 aluminum alloy	0088 ^b	5.7813	14.9	4.25	Total	38.0
0043	6061-T6 aluminum alloy	0088	5.9048	14.9	4.25	Total	21.0
0139	6061-T6 aluminum alloy, brazed joint	--	5.2895	13.4	3.9	2/3	19.5
0151	Control	--	--	--	3.75	--	10.0
0151*	Control (without gage)	--	--	--	3.75	--	--
0152	Control	--	--	--	3.75	--	6.0
0152*	Control (without gage)	--	--	--	3.75	--	--
0153	Control	--	--	--	3.75	--	14.5
0153*	Control (without gage)	--	--	--	3.75	--	--
0154	Control	--	--	--	3.75	--	6.0
0154*	Control (without gage)	--	--	--	3.75	--	--
0209	6Al-4V titanium-ELI	0093	9.0290	14.4	2.6	2/3	9.0
0210	1) 6Al-4V titanium-ELI 2) 6061-T6 aluminum alloy	0093	9.0378	14.4	2.6	2/3	10.0
		0088	5.8698	14.9	2.6	2/3	
0212	6Al-4V titanium alloy	0093	9.1093	14.6	2.6	2/3	16.0
0213	1) 6Al-4V titanium alloy 2) 6061-T6 aluminum alloy	0093	9.7220	14.4	2.6	2/3	10.0
		0088	5.8953	14.9	2.6	2/3	
0215	5Al-2.5Sn titanium alloy	0093	9.0670	14.4	2.6	2/3	27.5
0216	1) 5Al-2.5Sn titanium alloy 2) 6061-T6 aluminum	0093	9.0670	14.4	2.6	2/3	36.0
		0088	5.8910	14.9	2.6	2/3	
0218	5Al-2.5Sn titanium-ELI	0093	9.0673	14.4	2.6	2/3	8.0
0219	1) 5Al-2.5Sn titanium-ELI 2) 6061-T6 aluminum alloy	0093	9.0695	14.4	2.6	2/3	19.5
		0088	5.8951	15.1	2.6	2/3	
0221	6Al-6V-2Sn titanium ^c	0093	9.2173	14.7	2.6	2/3	11.0
0222	1) 6Al-6V-2Sn titanium ^c 2) 6061-T6 aluminum alloy	0093	9.2151	14.5	2.6	2/3	5.5
		0088	5.8921	14.9	2.6	2/3	
0224	6Al-6V-2Sn titanium ^d	0093	9.2023	14.6	2.6	2/3	11.0
0225	1) 6Al-6V-2Sn titanium ^d 2) 6061-T6 aluminum alloy	0093	9.2020	14.7	2.6	2/3	13.0
		0088	5.8295	14.9	2.6	2/3	
0237	6061-T6 aluminum alloy	0088	6.8087	15.9	2.4	9/10	25.0
0239	Control for 0237; reference for 0209-0225	--	--	--	2.4	--	17.0
0241	Control for 0237; reference for 0209-0225	--	--	--	2.4	--	39.5

a) All samples cleaned according to JPL Log No. 0087 and passivated according to listed Log Nos. See Appendix A for details.

b) NaOH treated.

c) Annealed

d) Ht-treated to 160,000 psi.

Table 3

IDENTIFICATION OF JPL STORAGE TESTS IN HYDRAZINE-UDMH:
TREATMENT, DIMENSIONS, AND STORAGE DATA

JPL TEST NO.	MATERIAL	PASSIVATED ^a JPL LOG NO.	WEIGHT, g	AREA, cm ²	STORAGE TIME, yr	DEPTH OF IMMERSION	FINAL STORAGE PRESSURE AT 110°F, psia
0263	6Al-4V titanium alloy	0093	9.4237	14.8	1.8	4/5	25.0
0263A	Control	--	--	--	1.8	--	12.5
0264	6Al-4V titanium alloy	0093	9.5911	14.9	1.8	4/5	7.5
0265	6Al-4V titanium alloy	0093	9.5670	14.9	1.8	4/5	11.5
0266	6Al-4V titanium alloy	0093	9.4792	14.8	1.8	4/5	15.5
0267	6Al-4V titanium alloy	0093	9.4661	14.9	1.8	4/5	10.0
0268	6Al-4V titanium alloy	0093	9.5921	14.9	1.8	4/5	15.0
0269	6Al-4V titanium alloy	0093	9.4422	14.8	1.8	2/3	13.0
0269A	Control	--	--	--	1.8	--	33.5
0271	6Al-4V titanium alloy	0093	9.4649	14.8	1.8	2/3	23.0
0272	6Al-4V titanium alloy	0093	9.1547	14.7	1.8	2/3	8.0
0273	6Al-4V titanium alloy	0093	9.5943	14.9	1.8	2/3	16.5
0274	6Al-4V titanium alloy	0093	9.0708	14.5	1.8	2/3	8.5

^{a)} All specimens cleaned according to JPL Log No. 0087 and passivated according to listed Log Nos.
See Appendix A for details.

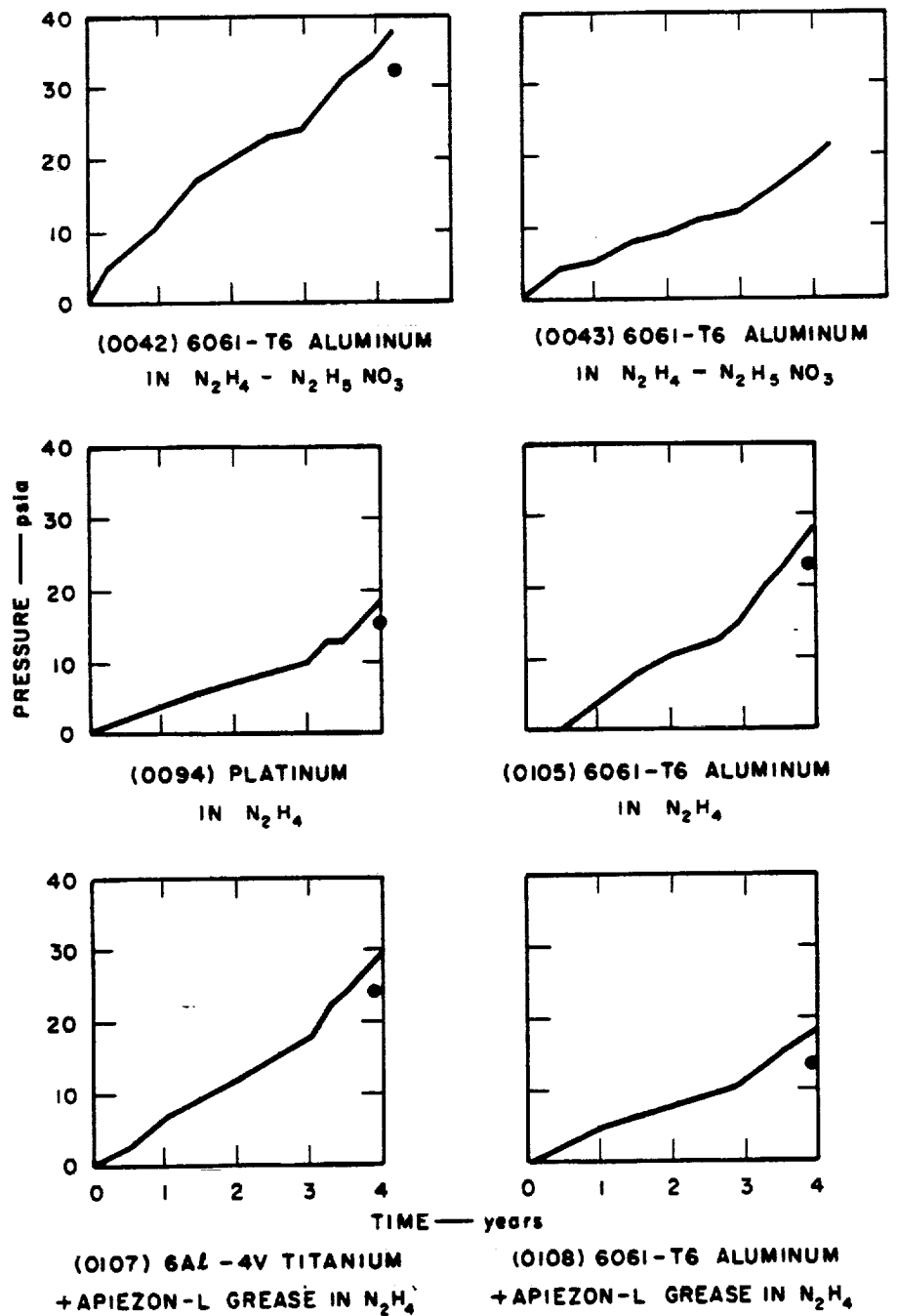
Table 4
INITIAL ANALYSES OF AMINE FUELS USED
IN JPL STORAGE TESTS

FUEL	JPL TEST NOS.	COMPOSITION, Wt.-%				
		N ₂ H ₄	C ₆ H ₅ NH ₂	NH ₃	HNO ₃	UDMH
Hydrazine	0094	--	--	--	--	--
	0105-0138	98.6	0.4	0.15	--	--
	0155	99.2	0.38	--	--	--
	0179-0181	97.9	--	--	--	--
	0243-0245	98.6	--	--	--	--
Hydrazine-Hydrazine Nitrate	0042-0139	82.6	0.4	0.6	15.9	--
	0151-0154	82.1	0.4	0.6	15.9	--
	0151*-0154*	82.1	0.4	0.6	15.9	--
	0209-0225	83.3	0.3	0.3	15.6	--
	0237-0241	83.3	--	--	15.6	--
Hydrazine-UDMH	0236-0274	50.8	--	--	--	48.5



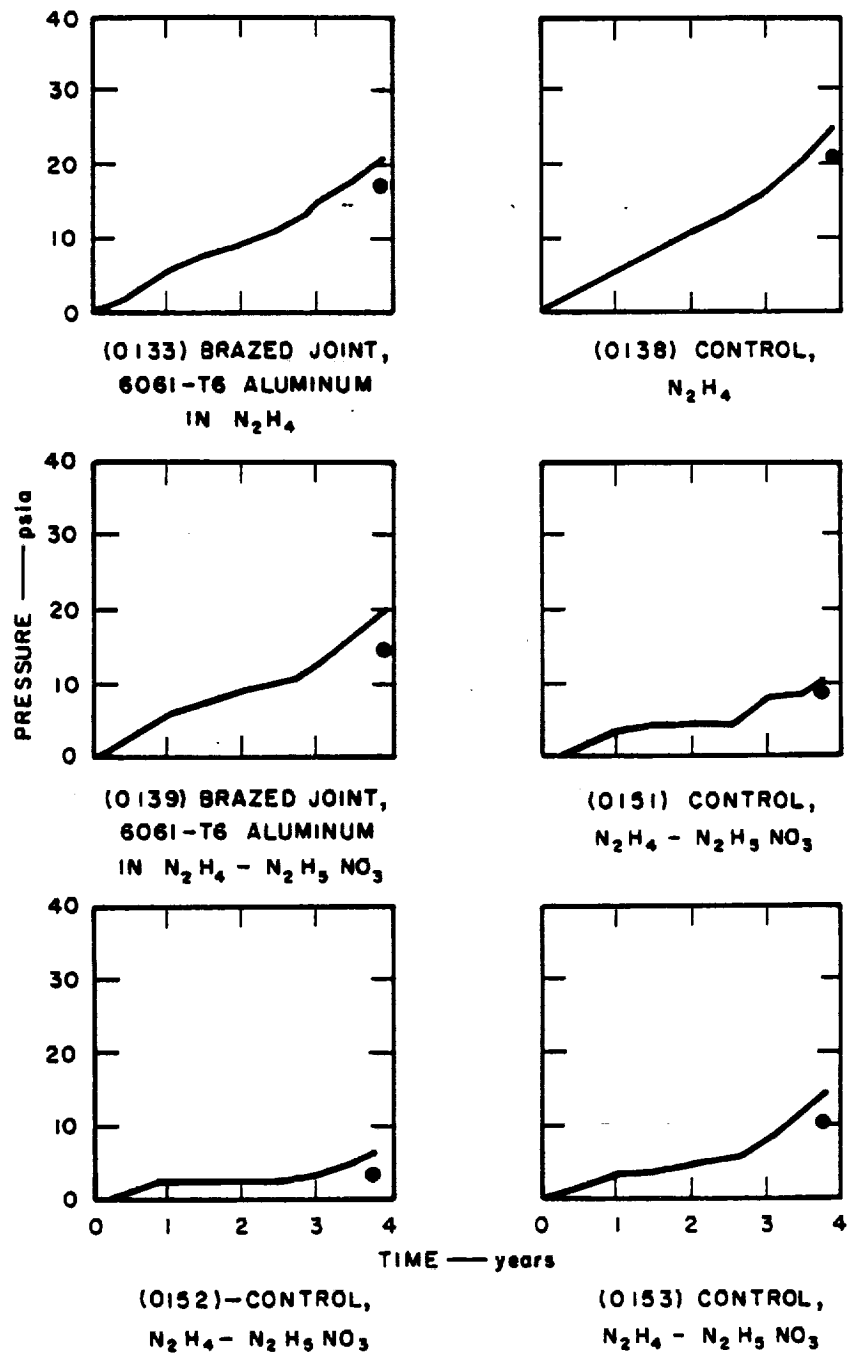
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FIG. 1 CLOSE-UP VIEW OF STORAGE CAPSULE (JPL) SHOWING
TYPICAL SPECIMEN AND AMINE FUEL CONTENT



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FIG. 2 PRESSURE DATA FOR JPL STORAGE TEST NOS. 0042 TO 0108



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FIG. 3 PRESSURE DATA FOR JPL STORAGE TEST NOS. 0133 TO 0153

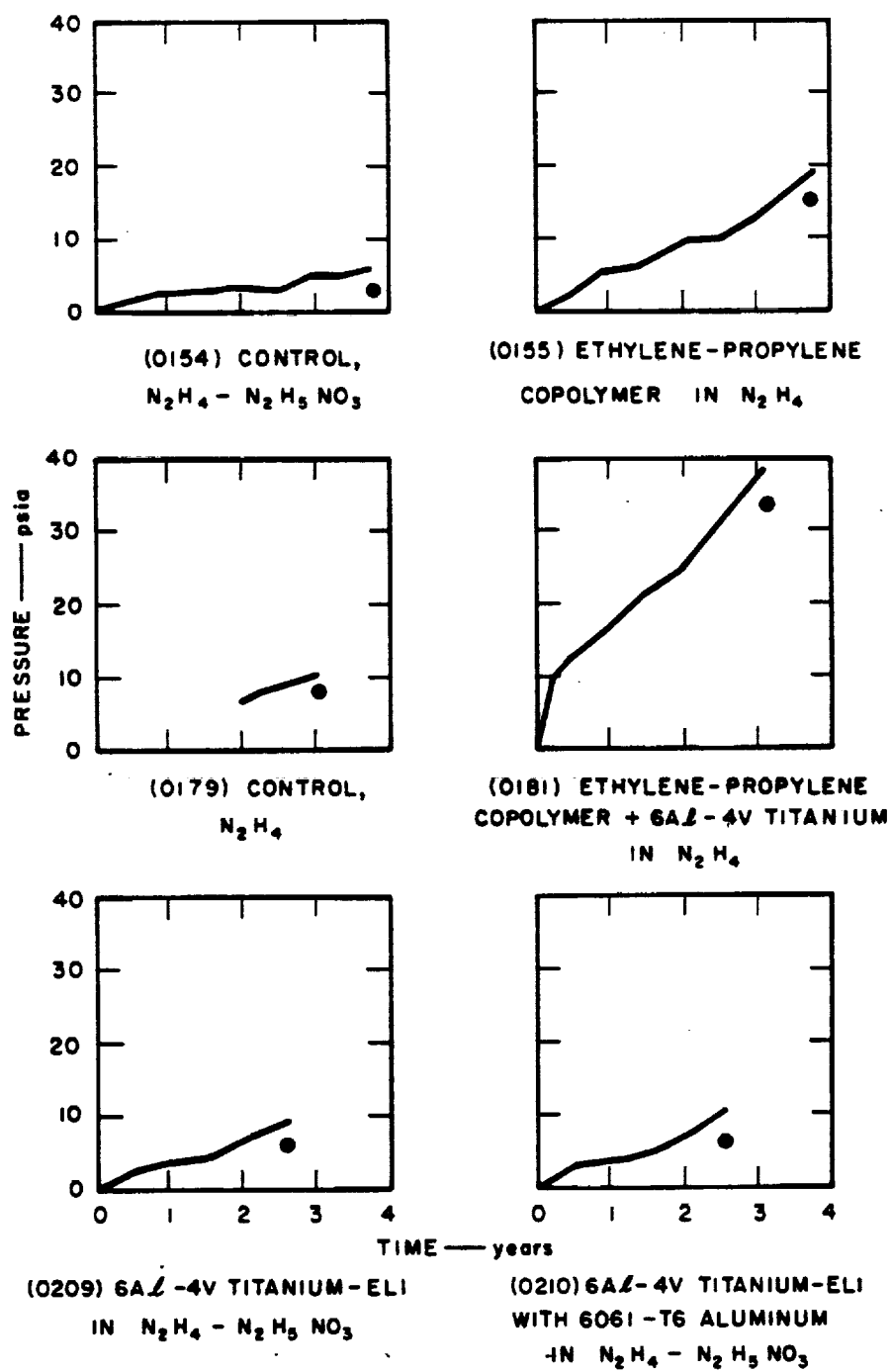


FIG. 4 PRESSURE DATA FOR JPL STORAGE TEST NOS. 0154 TO 0210

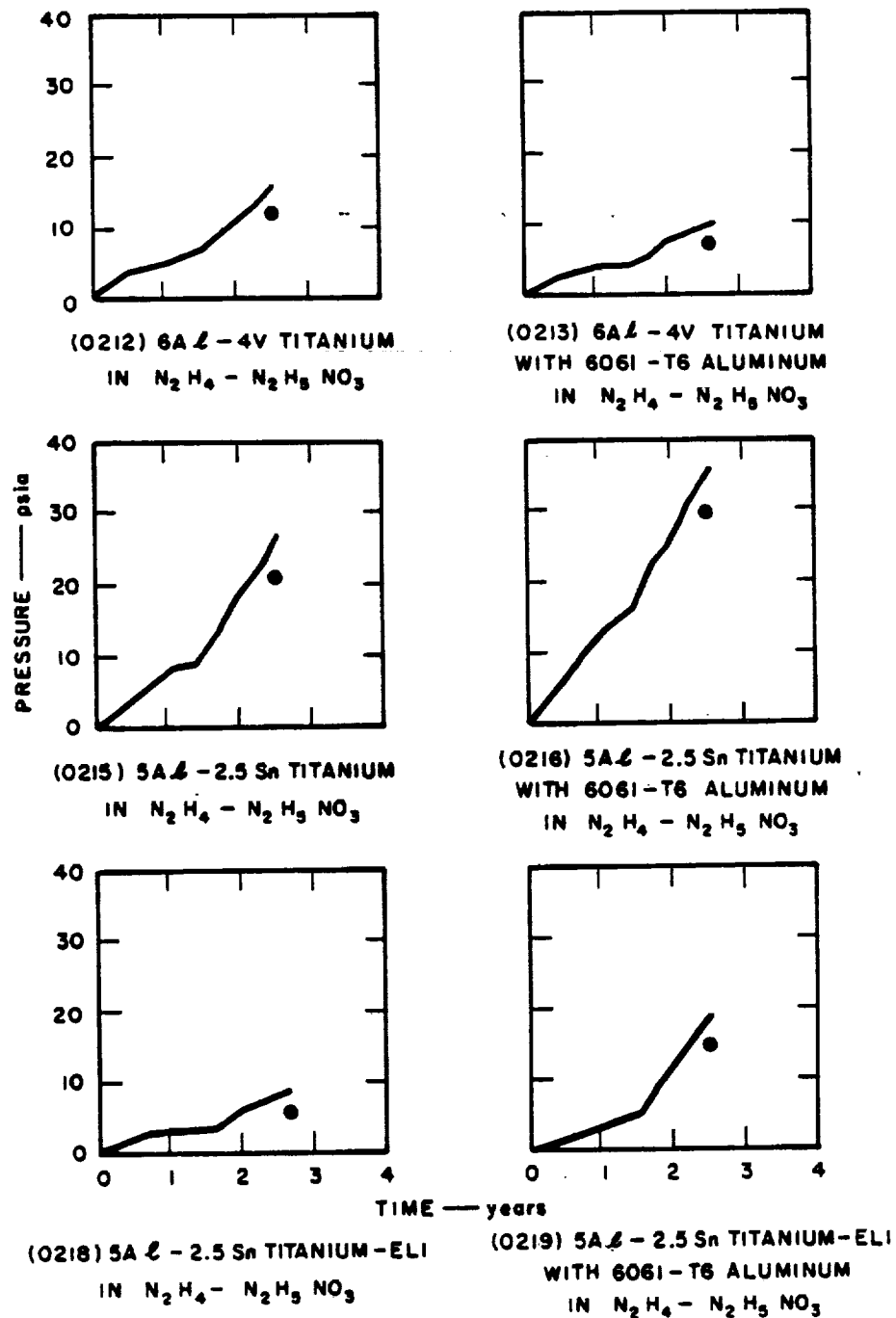
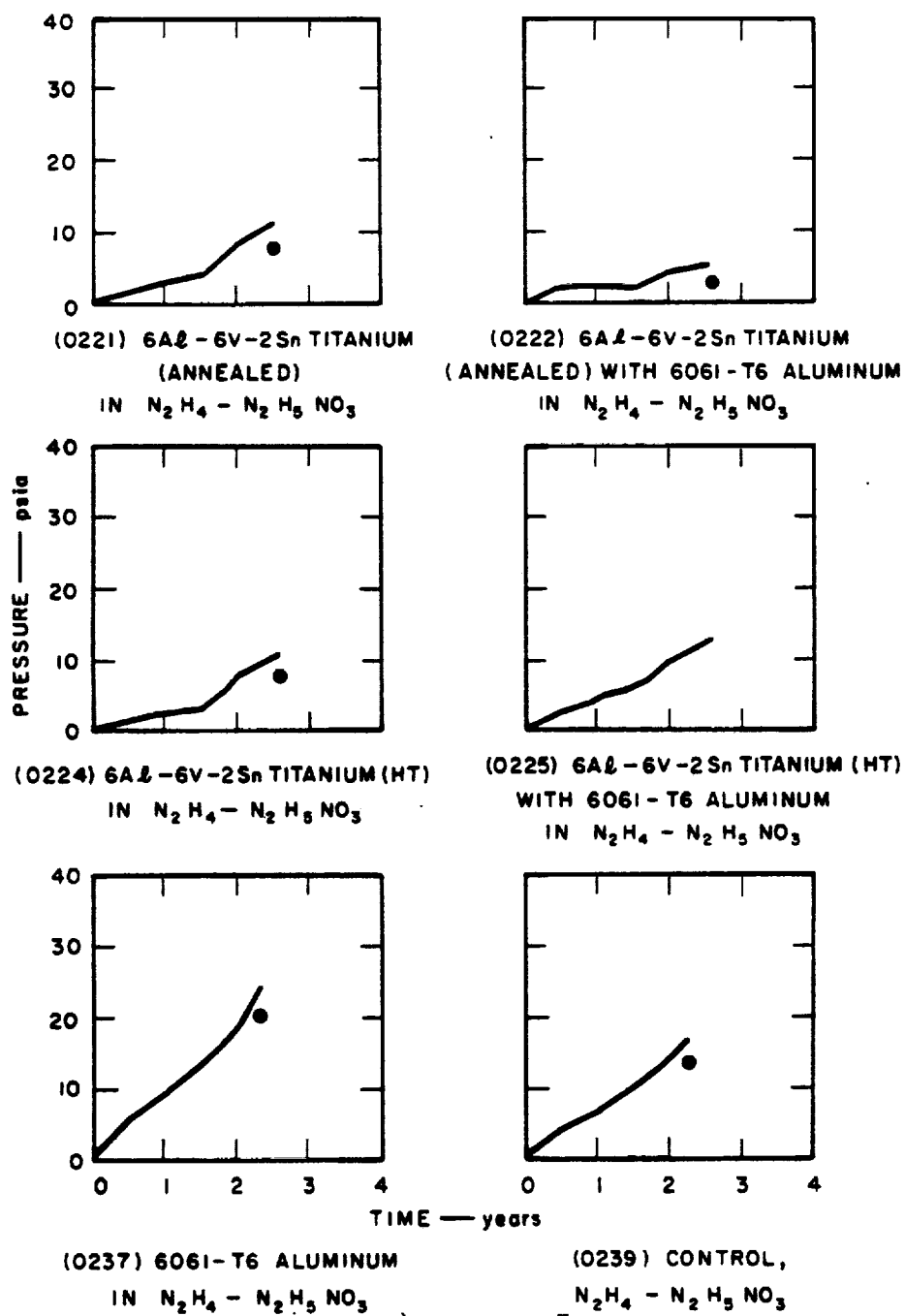


FIG. 5 PRESSURE DATA FOR JPL STORAGE TEST NOS. 0212 TO 0219



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FIG. 6 PRESSURE DATA FOR JPL STORAGE TEST NOS. 0221 TO 0239

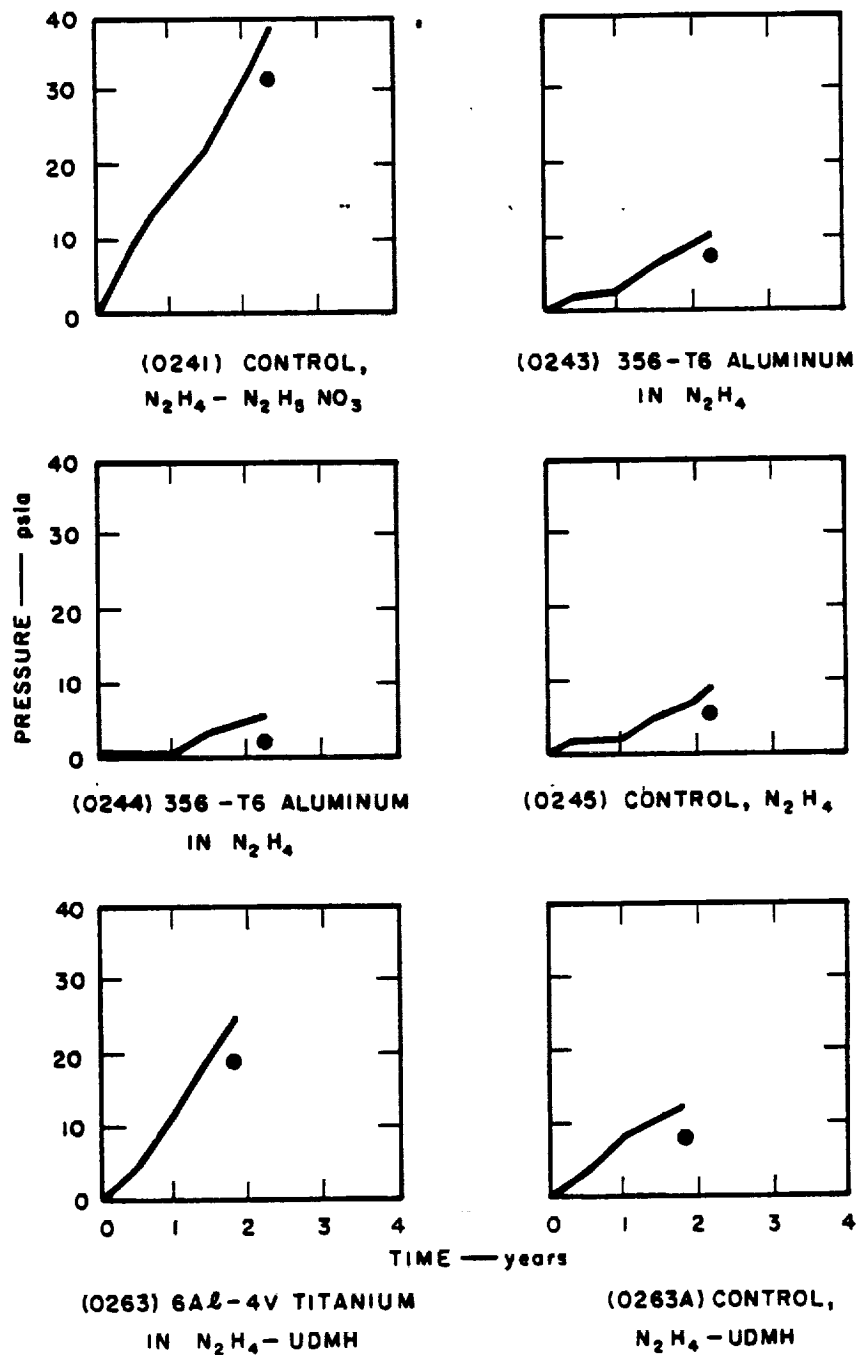


FIG. 7 PRESSURE DATA FOR JPL STORAGE TEST NOS. 0241 TO 0263A

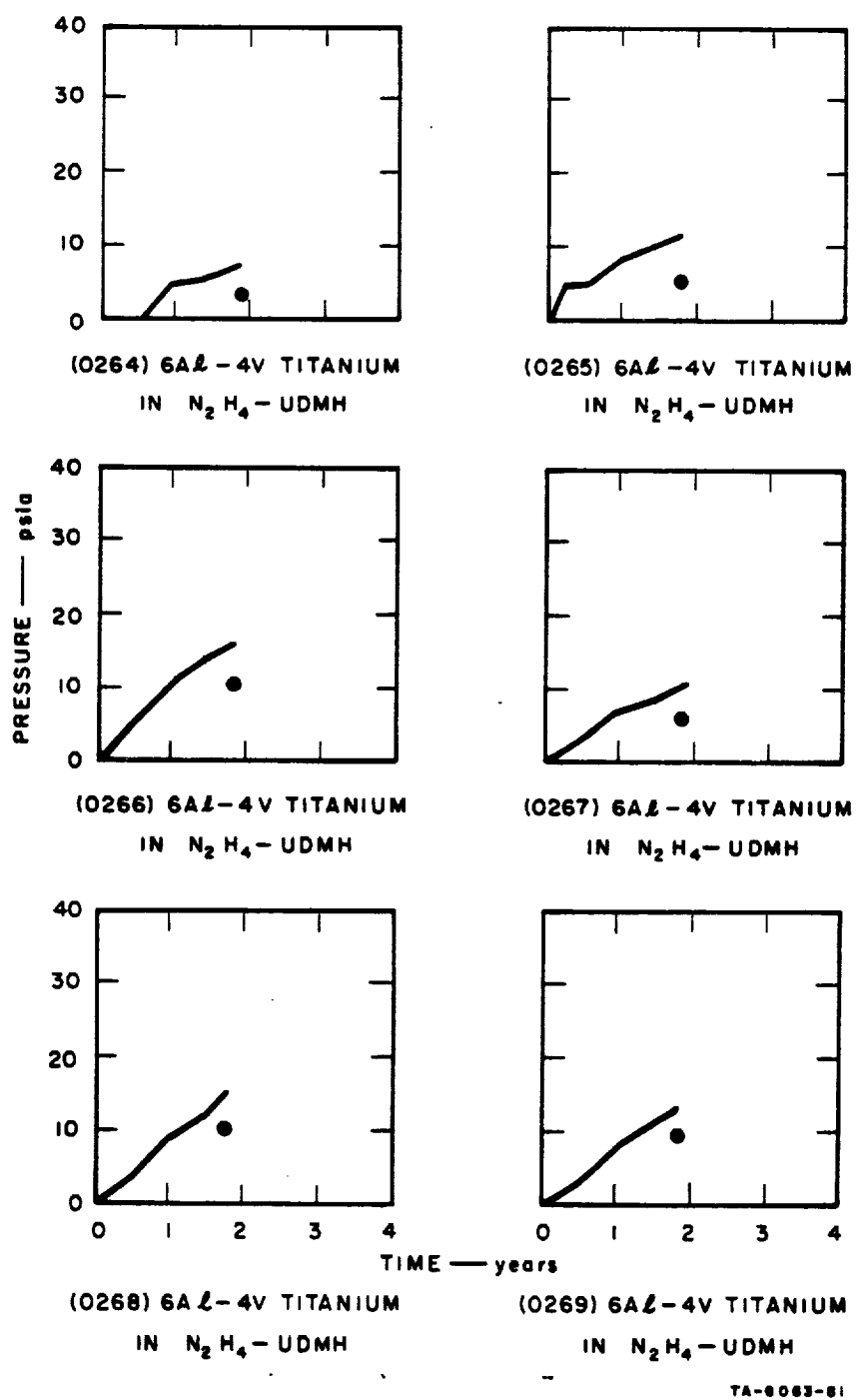
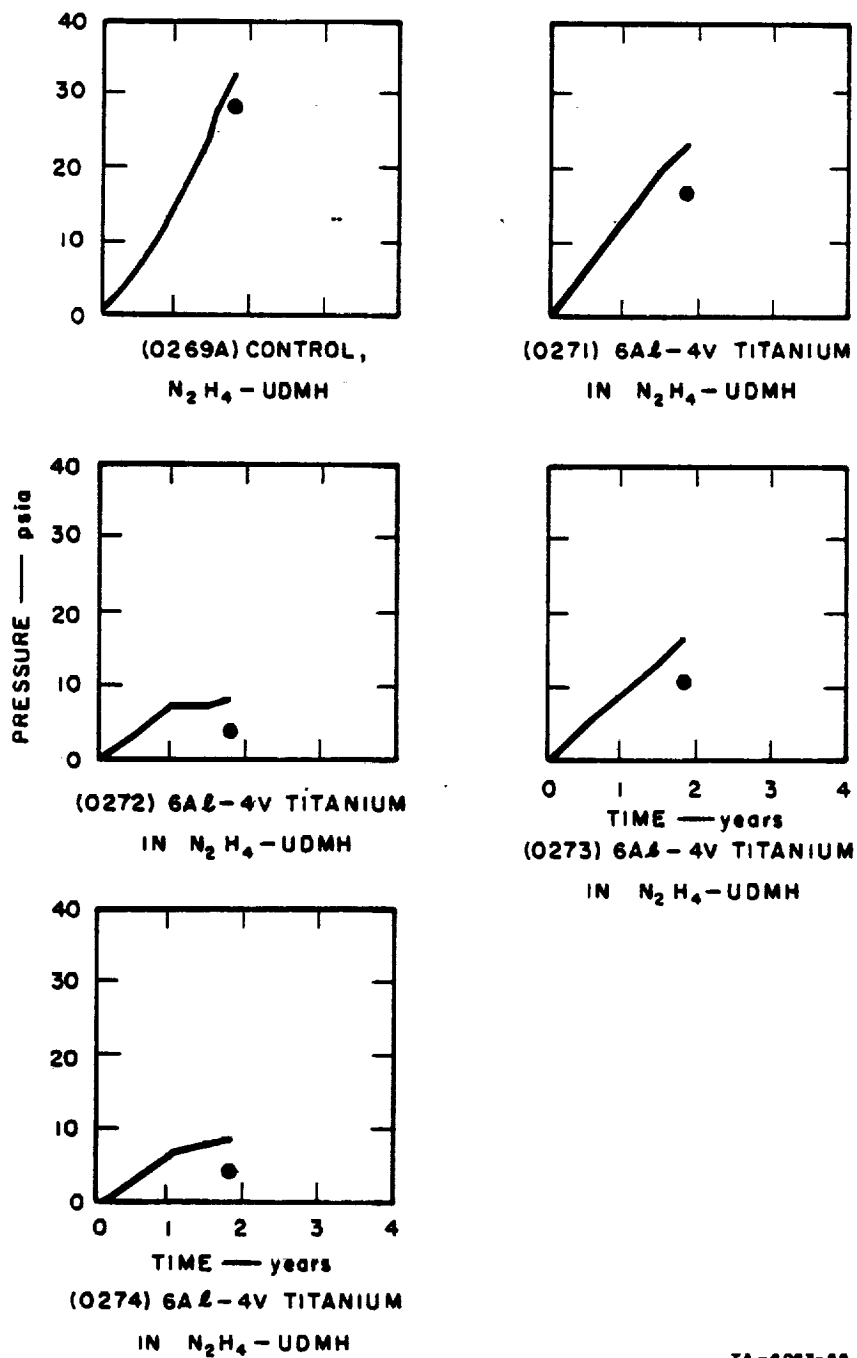
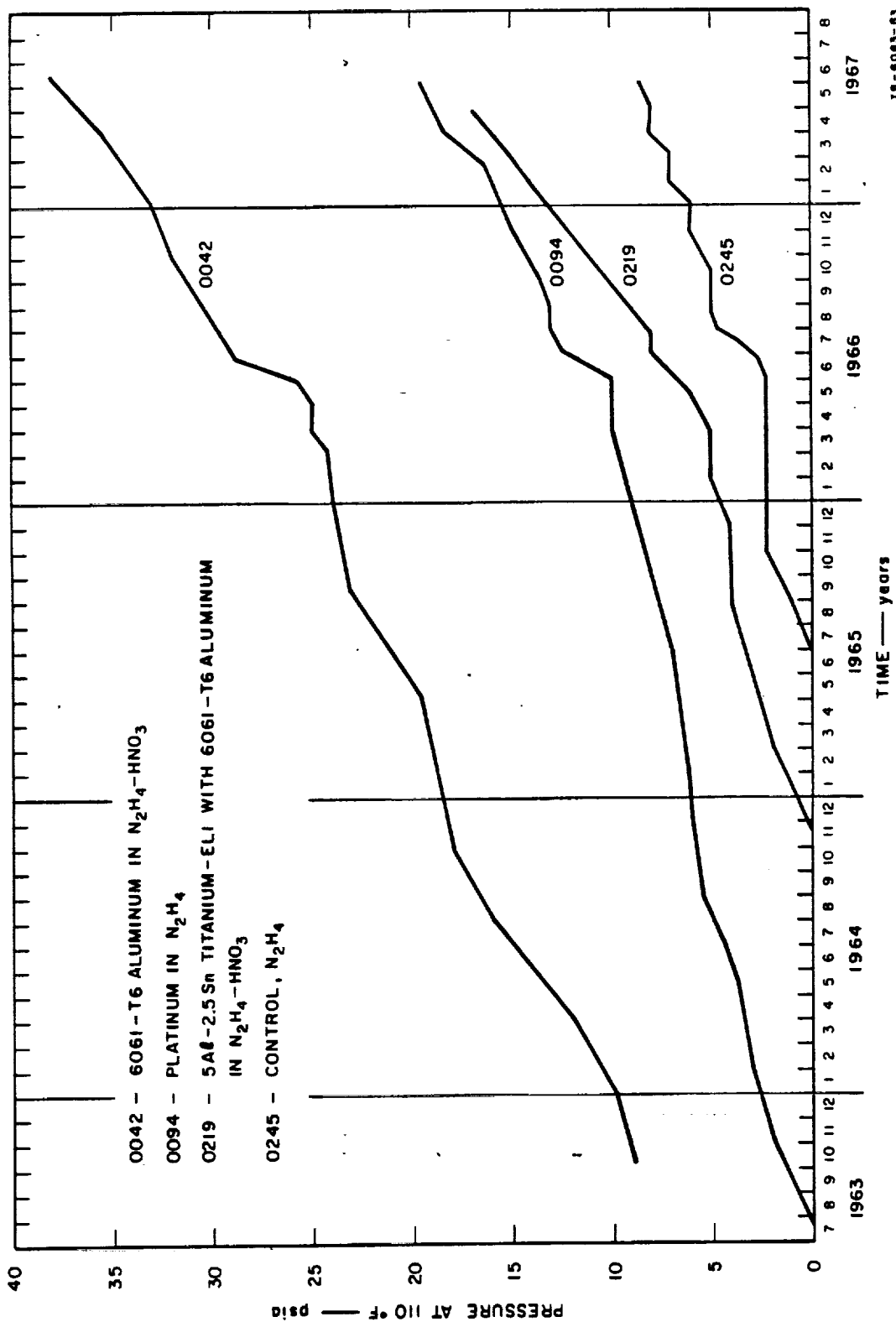


FIG. 8 PRESSURE DATA FOR JPL STORAGE TEST NOS. 0264 TO 0269



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FIG. 9 PRESSURE DATA FOR JPL STORAGE TEST NOS. 0269A TO 0274



18-6063-63

FIG. 10 VAPOR PRESSURES OF SEVERAL STORAGE TESTS SELECTED AT RANDOM TO ILLUSTRATE THE ABRUPT PRESSURE CHANGE IN ALL TESTS AT ABOUT THE SAME CALENDAR TIME

III. ANALYTICAL PROCEDURES

The storage capsules received at SRI were removed from the dry-ice/Vermiculite packing in which they were shipped, wiped with isopropyl alcohol to remove condensed water, and stored in a freezer at -25°C . After the capsule pressures had equilibrated at this temperature, the gage pressures were recorded. The capsules were then immersed in liquid nitrogen to above the neck and the gage pressures were recorded at -196°C ; the pressure at this temperature is an indication of the presence of permanent gases (N_2 , H_2 , O_2) in the ullage volume, since all other probable components would have essentially zero pressure. (The lowest pressure which can be read on the gages used is 1 psia; therefore, any pressure lower than this would be read as 0 psia.) The capsules were warmed to room temperature (22°C), the gage reading was recorded, and the fuel and specimens were inspected for color, sediment, or any unusual features.

The capsules were wiped dry of condensed moisture and placed in a helium-filled glove box so that they could be opened in a dry and inert atmosphere. They were first opened at the Swagelok fitting and a portion of the ullage gas was removed for analysis. The neck of the glass capsule was broken and the fuel was transferred into a weighed sample bottle which was re-weighed and stored at -25°C in order to obviate any further decomposition of the fuel.

Finally, the specimen was removed from the capsule, dried under a heat lamp in a helium atmosphere, and stored in a capped bottle for later examination; the specimens which had been stored in hydrazine-hydrazine nitrate mixture were rinsed with hydrazine before drying (to remove acidic residues which might invalidate observations of corrosion that took place during storage).

The ullage volume was determined as the difference between the volume of the emptied capsule filled with a weighed amount of water and the volume (from weights) occupied by the fuel and the specimen.

After the capsules were opened and the gages exposed to the atmosphere, the gage readings were noted. All gages, except two, read 14.7 psia within a few tenths of a pound, which indicates that the gage readings during storage were correct and that the gages were originally adjusted to read in psia. The two which did not read correctly were those on capsules 0264 and 0273, which read 11.6 and 13.8 psia, respectively; the capsules contained 6Al-4V titanium alloy in hydrazine-UDMH mixture.

FUEL ANALYSES

The fuel samples in weighing bottles were removed from the freezer and warmed to room temperature just prior to analysis.

Water Content

The water content of the hydrazine and hydrazine-hydrazine nitrate fuels was determined by titration with Karl Fisher reagent, using 3:1 methanol:glacial acetic acid as a solvent. The water in the solvent was titrated to an end point, about one gram of sample was added from a weighed, stoppered syringe, and the solution was titrated rapidly to the final end point (dead-stop).

A gas chromatographic method was used to determine the water content of the hydrazine-UDMH mixtures. The column was made of aluminum tubing (1/8-in diameter and 40-in long) packed with Poropak-R, 50-80 mesh, and was operated at 100°C. Helium was used as the carrier gas at a flow rate of 60 cc/min. Standards were prepared by adding known amounts of water to 50% mixtures (w/w) of propellant-grade hydrazine and UDMH which had been dried by distillation over potassium hydroxide pellets.

Aniline

The aniline content of all the fuel samples was determined by ultraviolet spectrophotometry. A weighed sample of about 1 gram was dissolved in methanol, diluted to volume in a 100-ml flask, and transferred to a 1-cm cuvette. The absorbance at 285 mμ was measured with a Cary Model 14M spectrophotometer and compared with standards prepared from reagent-grade aniline.

Ammonia

The method of Wiebke [Anal. Chem., 23, 922 (1951)] was used for the determination of ammonia in the hydrazine and hydrazine-hydrazine nitrate fuels. In this procedure, the major part of the hydrazine is precipitated as a poorly-soluble salt, $\text{CuSO}_4 \cdot (\text{N}_2\text{H}_5)_2\text{SO}_4$, which is removed by filtration; the remaining hydrazine is oxidized to nitrogen by Fehling's solution. The ammonia is then distilled into dilute boric acid and titrated with standard acid.

No satisfactory method was found for the determination of ammonia in hydrazine-UDMH mixtures.

Nitric Acid

The nitrate content of hydrazine-hydrazine nitrate mixtures was determined by Devarda's method. Subsequent to the distillation of ammonia as described in the above procedure, several grams of Devarda's alloy were added to the alkaline solution remaining in the stillpot; after standing at room temperature for about 20 minutes to allow reduction of the nitrate to ammonia, the solution was diluted with about 150 ml of water and the ammonia was distilled over into dilute boric acid and titrated with standard acid to a colorimetric end point.

Residue

After all other analyses had been completed, the nonvolatile content of the propellents was determined by evaporating about 5 ml of hydrazine or hydrazine-UDMH mixture in a platinum crucible at 100°C and weighing

the residue. The crucible was then ignited at 500°C to destroy any organic matter and to convert any metal salts to oxides and re-weighed. The residue at 100°C is an indication of the amount of organic material dissolved or dispersed in the sample. Of course, any organic matter which is volatile at 100°C would not be detected.

For the hydrazine-hydrazine nitrate mixtures, the residue at 100°C would consist largely of nonvolatile hydrazine nitrate; thus, only the residue at 500°C was determined. To avoid any violent decomposition of the hydrazine nitrate, the sample first was heated gently to evaporate most of the hydrazine. Then the crucible was cooled, and a small amount of water and 1 ml of 1:1 sulfuric acid was added. Finally, the crucible was heated carefully until all of the salts had decomposed and the sulfuric acid had evaporated; then it was ignited cautiously at 500°C and re-weighed.

Hydrazine

The hydrazine content of samples containing hydrazine only or hydrazine-hydrazine nitrate was determined by titration with chloramine-T, using the procedure described in JPL Spec. No. GMZ-50521-GEN-A. Because the reaction of chloramine-T with UDMH is not stoichiometric, this procedure was not used for hydrazine-UDMH mixtures.

Hydrazine-UDMH Mixtures

These fuels were analyzed for hydrazine and UDMH by nonaqueous acid-base titration using the method of Malone and Biggers [Anal. Chem., 36, 1037 (1964)]: A weighed portion of sample is diluted in a volumetric flask in glacial acetic acid. One aliquot of this solution is titrated for total basicity using standardized perchloric acid in glacial acetic acid; quinaldine red is used to detect the end point. To a second aliquot, a few ml of acetic anhydride are added. After standing one minute, this solution is titrated also with standardized perchloric acid to the same end point. In the latter treatment, hydrazine, but no UDMH, is acetylated rapidly to form a neutral product so that the second titration is

a direct measure of the UDMH content of the sample. The amount of hydrazine is calculated from the difference between the two titrations.

The major interferences in this procedure are ammonia and aniline. Ammonia is titrated along with the UDMH so that the value obtained is actually UDMH plus the ammonia content. Aniline was found to acetylate rapidly and thus is included in the hydrazine value; however, since the aniline can be determined independently, an appropriate correction can be made.

SPECIMEN ANALYSES

Weight Change and Corrosion Rate

The specimens were weighed on an analytical balance to ± 0.2 mg and the weights were compared with the original values provided by JPL. Then, the specimens were cleaned by washing with distilled water while rubbing with a soft cloth, dried, and re-weighed. Corrosion rates were calculated by using the weight changes from initial weights after cleaning, and it was assumed that corrosion had taken place uniformly over the entire surface of the specimen.

Because of the small amount of corrosion and correspondingly small weight changes expected, great care was taken in weighing the specimens. The balance used (Mettler Grammatic) was carefully adjusted and frequently checked against a set of N.B.S. certified weights (Class M). There is always a question of accuracy when weighings are made by different operators on different balances, and the expected error in this case would be about ± 0.2 mg.

Microscopy and Photography

All specimens were examined under a microscope for evidence of corrosion or any irregular features and special note was taken of the appearance of the interfaces.

It was possible that the aniline present in the fuels might react with the fuel or specimens to form polymeric aniline black which is highly fluorescent. Thus, all specimens were examined under ultraviolet light for evidence of any fluorescent deposit or coating, but none was found.

Full-size photographs were taken of all specimens immediately following their removal from the storage capsules in order to record their original appearance. For the specimens which showed evidence of corrosion or other attack, photomicrographs of the flat ends were taken on Polaroid film (PN55) with a Graflex 4 x 5 camera. Where photographs of interfaces, welded joints, etc. were required, photomicrographs were taken at low magnification in order to obtain depth of field and the final prints were enlarged for publication.

ULLAGE GAS ANALYSES

In many instances, the gage pressures of the storage capsules registered more than one psia at liquid nitrogen temperature. In order to determine whether the noncondensable gases were a result of trapped air (or air leakage during storage) or were really the result of amine fuel decomposition, these ullage gases were sampled for mass spectrometric analysis.

As indicated earlier, the storage capsules were opened at about 25°C in a dry-box containing an atmosphere of helium. Prior to opening the storage capsules, gas-sampling vessels of about 250-ml volume were evacuated to 10^{-6} torr and placed in the dry box with sampling needles (1/16" stainless steel tubing) which could be attached easily to the gas vessels by means of short lengths of plastic tubing. When a capsule was opened, the sampling needle attached to the gas vessel was inserted down the bore of the neck of the capsule nearly to the liquid surface, the gas vessel stopcock was opened so that the mixture of ullage gases and helium could be withdrawn into the gas vessel, and then the stopcock was closed. By this procedure, there was little chance of air contamination

from sampling techniques. Frequent analyses of the dry-box atmosphere indicated that less than a few per cent of air was present during sampling.

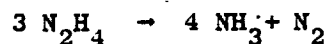
After sampling and removal from the dry-box, a gas vessel was attached to the 3-liter gas inlet system of a Consolidated Electrodynamic Corporation mass spectrometer, Model 21-103C. Since only the presence and proportions of noncondensable gases are of significance for determining the nature of the gases contributing to gage pressures at -195°C , the gas vessel was cooled to liquid nitrogen temperature to condense out water, amine fuels, ammonia, etc. and thus duplicate the conditions of pressure measurement at -195°C . Then, standard procedures were followed for the quantitative determination of the ullage-gas composition, including introduced helium.

The mol-ratio of nitrogen/hydrogen was computed to be used for final calculations of the amounts of hydrogen and nitrogen formed by amine fuel decomposition. The air content of the gas samples was computed from the argon content; it was found that insufficient oxygen was present for the amount of air indicated, and thus the mol-% of oxygen consumed in the fuel decomposition was calculated. The air providing this oxygen probably was residual air present when the capsules were sealed.

IV. RESULTS OF STORAGE TESTS WITH HYDRAZINE

The results of the storage tests indicate that the materials most compatible with hydrazine in a sealed system at 110°F are platinum, 6061-T6 aluminum alloy, and ethylene-propylene co-polymer. Noncompatible materials appear to be 6Al-4V titanium alloy, 356-T6 aluminum alloy, and either the fluorocarbon, Rulon, or the combination of Rulon with 6061-T6 aluminum. Corrosion of all specimens is limited to staining and all calculable corrosion rates are less than 1 microinch per year. A summary of corrosion rates (computed after storage) and of compatibilities (computed from hydrazine decomposition during storage) is given in Table 5.

Photographs of the test specimens as received are given in Figs. 11 to 14, and the analysis of the specimens is found in Table 6. The results of the analyses for hydrazine and ullage gases are recorded in Tables 7 and 8, respectively. Based on the storage data provided by JPL and the data in Table 8, a normalized (to constant ullage) decomposition-rate curve for hydrazine has been plotted in Fig. 15, and normalized pressure data for the storage tests with various specimens are summarized in Table 9. The compatibility ratings are based primarily on comparison of the normalized pressures in Fig. 15 with the pressures given in Table 9. The development of the pressure appears to be due to the decomposition of hydrazine during storage according to the equation:



This is confirmed by an analysis of the data for fuel compositions, non-condensable gas compositions, terminal storage pressures, and ullage volumes.

A detailed discussion of the mode of decomposition is given in the concluding Section of this report.

Compatibility with hydrazine implies not only a minimum of corrosion but also that the specimen has not caused an increase in the normal decomposition rate established for hydrazine during the period of storage at 110°F. The pressure values recorded suggest that the normal decomposition rate for hydrazine is about 0.4% over a 4-year period; thus, if only ammonia and nitrogen are formed:

In a capsule containing 40 g of hydrazine and having a 40-cc ullage volume, if 0.4% of the hydrazine decomposed, about 0.28% ammonia would be added to the original ammonia in solution and about 1.66 millimoles of nitrogen would be liberated into the ullage volume. The nitrogen would create a pressure of about 15.6 psia at 110°F and about 3.84 psia at -196°C. (These values are close to the average values in Table 8.)

Referring to Fig. 11 and Table 6, no evidence of corrosion, such as etching or pitting, was noted for the metallic specimens when examined microscopically. The staining of the specimens was largely at the interface and in the areas exposed to the vapor phase. The weight changes of all specimens were less than 1 mgm, even after cleaning. The small increases in weight for four of the specimens may be due to differences in weighing techniques and the absorption of water; nevertheless, the weight changes do not indicate corrosion rates of greater than 1 μ inch/year. In all instances, about 1% (or more) water was present in the initial hydrazine (estimated from incomplete analytical data, Table 4), and increased during storage by about 1/2% (Table 7). The apparent increase may be due largely to the inaccuracy of either the original or the final analysis; however, it is shown by mass spectrometric analysis (see Part III) of the noncondensable ullage gases (Table 7) that oxygen (as air) was present initially and consumed during storage, and thus there is the possibility of oxidation of hydrazine and the concomitant formation of water. Unfortunately, no firm theories can be vouchsafed since these conjectures are based on an accumulation of single determinations on single samples coupled with initial assumptions and reliance on pressure measurements.

A water content greater than average is shown for the hydrazine after storage with 6061-T6 aluminum coated with a sprayed-on fluorocarbon, Rulon (0105); additionally, the pressures developed in this storage test are excessive (see normalized data, Table 9). It might be assumed that the Rulon itself may have impurities that caused decomposition of the hydrazine, but it is also more probable that extraneous impurities might have been introduced prior to storage, as evidenced by the final excessive water content. Impurities must be suggested since 6061-T6 by itself or with a grease appears to be quite compatible with hydrazine. Hence, the results of the test with 6061-T6 and Rulon remain questionable.

In another example of correlations leading to decisions for compatibility ratings, the data indicate that the co-polymer ethylene-propylene (0155) is compatible with hydrazine but not in combination with 6Al-4V titanium. Apiezon-L grease with 6061-T6 aluminum (0108) is compatible with hydrazine, but in combination with 6Al-4V titanium (0107) it is not. On the basis of the test results, it perhaps is appropriate to conclude that 6Al-4V titanium is not compatible with hydrazine.

The EPR bonded to 6Al-4V titanium (0181) was found unbonded when the capsule was disassembled. It was at first considered at the bonding adhesive was responsible for incompatibility but, as suggested above, it is highly probable that loss of bond occurred because the titanium alloy is incompatible. The EPR itself (0155) suffered little from exposure to hydrazine. Final Shore hardness ("A" scale) was 86.4 for 0155 and 86.0 for 0181; this is favorably-contrasted with an independent reading for a similar EPR (E515-8 O-ring) of 82.7. (Initial hardness measurements of the stored specimens were not provided.) Although the EPR (0155) was "set" in the shape it assumed during storage as shown in Fig. 12, (typical of polymeric materials stored in fixed positions),

it was still flexible and elastic.* The staining of the titanium at the adhesive bond (0181) is easily visible in Fig. 13.

Discoloration of hydrazine was observed in the storage tests with EPR (0155 and 0181), probably due to extraction of extraneous organic matter, and with the 6061-T6/brazed joint specimen (0133), possibly due to the presence of brazing flux (or very small amounts of metallic salts). A magnified portrayal of the 6061-T6 brazed joint is shown in Fig. 14; however, the jointed specimen appears to be compatible with hydrazine.

* The determination of the permeability of the EPR to hydrazine after storage was considered; however, the sample strips of 1/2" width were not amenable with the presently available permeability fixture which requires a sample of at least 1-1/2" diameter. These determinations will be made at a future date.

Table 5
RESULTS OF JPL STORAGE TESTS: CORROSION RATES
AND COMPATIBILITIES WITH HYDRAZINE

JPL TEST NO.	MATERIAL	STORAGE TIME, YR	CORROSION		COMPATIBILITY ^b			
			μ in/yr	Rating ^a	1 Yr	2 Yr	3 Yr	4 Yr
0094	Platinum	4.1	0.1	1	C	C	C	C
0105	6061-T6 aluminum + Rulon coating	3.9	0.1	1	C	?	?	?
0107	6Al-4V titanium + Apiezon-L coating	3.9	1.0	1	C	NC	NC	NC
0108	6061-T6 aluminum + Apiezon-L coating	3.9	1.0	1	C	C	C	C
0133	6061-T6 aluminum, brazed joint	3.9	0.1	2	C	C	C	C
0243	356-T6 aluminum	2.2	1.0	1	C	NC	--	--
0244	356-T6 aluminum	2.2	1.0	1	C	NC	--	--

^a 1 = excellent, $< 1 \mu$ in/yr; attack limited to stain or extremely thin coating.

2 = good, $1-3 \mu$ in/yr; attack limited to stain or thin coating; no apparent etching or pitting.

^b C = Compatible; within limits of decomposition rate of hydrazine.

NC = Noncompatible; outside limits of decomposition rate of hydrazine.

Table 6
CORROSION OF VARIOUS MATERIALS STORED WITH HYDRAZINE

JPL TEST NO.	MATERIAL	WEIGHT CHANGE, g	DEPTH OF IMMERSION	APPEARANCE	REMARKS
0094	Platinum	+0.0002	total	no indication of etch, pit, or stain	--
0105	6061-T6 aluminum + Rulon coating	-0.0004	2/3	Rulon coating irregular, no etch or pit, slight stain at interface	Rulon wt., init. 0.0030 g final 0.0027 g
0107	6Al-4V titanium + Apiezon-L coating	+0.0010	1/2	no pit, etch, or stain; grease coating intact	Apiezon wt., init. 0.0405 g final 0.0247 g
0108	6061-T6 aluminum + Apiezon-L coating	+0.0008	2/3	no pit or etch, slight spotty stain on vapor phase; grease coating intact	Apiezon wt., init. 0.0425 g final 0.0148 g
0133	6061-T6 aluminum, brazed joint	±0.0000	total	some etch and stain, apparently due to brazing flux only	--
0151	Ethylene-propylene co-polymer	--	total	no sign of swelling, some permanent set, still elastic	--
0181	Ethylene propylene co-polymer bonded to 6Al-4V titanium	--	total	polymer like 0151; metal not etched but stained at contact with polymer	adhesive failed during storage
0243	356-T6 aluminum	+0.0008	2/3	no pits or etch, some stain in vapor phase	--
0244	356-T6 aluminum	+0.0005	2/3	no pit or etch; some spotty stain, mostly in vapor phase	--

Table 7
ANALYSIS OF HYDRAZINE STORED WITH VARIOUS MATERIALS

JPL TEST NO.	MATERIAL	STORAGE TIME, YR	FUEL Wt., g	COMPOSITION, Wt-%				RESIDUE, Wt-%	
				N ₂ H ₄	C ₆ H ₅ NH ₂	H ₂ O	NH ₃	at 100°C	at 500°C
0094	Platinum	4.1	40.5	97.2	0.42	2.0	0.34	0.004	< 0.001
0105	6061-T6 aluminum + Rulon coating	3.9	19.6	96.0	0.43	2.8	0.83	0.015	< 0.001
0107	6Al-4V titanium + Apiezon-L grease	3.9	17.9	97.2	0.43	2.0	0.98	0.008	< 0.001
0108	6061-T6 aluminum + Apiezon-L grease	3.9	19.4	96.9	0.43	2.3	0.60	0.003	< 0.001
0133 ^a	6061-T6 aluminum, brazed joint	3.9	38.1	96.7	0.43	2.4	0.31	0.002	< 0.001
0138	Control for 0133	3.9	38.6	96.4	0.44	2.5	0.40	0.002	< 0.001
0155 ^a	Ethylene-propylene co-polymer	3.7	39.2	98.0	0.34	0.97	0.27	0.020	0.004
0179	Control for 0181	3.1	40.4	97.5	0.33	2.0	0.22	0.004	< 0.001
0181 ^a	Ethylene-propylene co-polymer + 6Al-4V titanium	3.1	40.2	97.8	0.34	0.85	0.55	0.020	0.004
0243	356-T6 aluminum	2.2	20.5	97.0	0.60	2.1	0.25	0.004	< 0.001
0244	356-T6 aluminum	2.2	20.7	97.4	0.58	1.9	0.26	0.004	< 0.001
0245	Control for 0243, 0244	2.2	19.9	97.4	0.62	2.1	0.30	0.004	< 0.001

^a Hydrazine was pale yellow-brown in color.

Table 8
ANALYSIS OF ULLAGE GASES OVER HYDRAZINE
STORED WITH VARIOUS MATERIALS

JPL TEST NO.	MATERIAL	STORAGE TIME, yr	ULLAGE VOLUME, cc	FINAL PRESSURE AT 110°F, psia	PRESSURE AFTER STORAGE, psia		NONCONDENSABLE GASES, mol- ratio N ₂ /H ₂	O ₂ CONSUMED, mol-ratio O ₂ /H ₂
					22°C	-25°C		
0094	Platinum	4.1	39	20.0	15.8	13.5	21.07	1.30
0105	6061-T6 aluminum + Rulon	3.9	55	27.5	23.2	19.5	14.52	1.26
0107	6Al-4V titanium + Apiezon-L grease	3.9	59	28.5	24.0	20.0	52.09	2.94
0108	6Al-4V titanium + Apiezon-L grease	3.9	55	17.5	13.6	12.0	24.13	1.21
0133	6061-T6 aluminum, brazed joint	3.9	38	21.0	17.0	13.0	37.91	2.85
0138	Control for 0133	3.9	41	25.5	21.0	16.5	12.30	0.61
0155	Ethylene-propylene co-polymer	3.7	35	19.0	15.0	13.0	22.55	1.77
0179	Control for 0181	3.1	43	10.5	8.0	7.0	17.48	2.02
0181	Ethylene-propylene co-polymer + 6Al-4V titanium	3.1	32	38.5	33.5	26.0	57.23	5.18
0243	356-T6 aluminum	2.2	52	10.0	7.3	7.0	13.68	1.89
0244	356-T6 aluminum	2.2	53	4.5	2.0	1.0	--	--
0245	Control	2.2	59	9.0	6.5	5.5	--	--

Table 9
DECOMPOSITION OF HYDRAZINE AS CONTROL SAMPLES
AND WITH STORED SPECIMENS (PRESSURE DATA)

JPL TEST NO.	PRESSURE (NORMALIZED TO 45-cc ULLAGE), psia				
	1 Yr	2 Yr	3 Yr	4 Yr	4 Yr (extr.) ¹
<u>N₂H₄ Controls</u>					
0138	5.5	10.0	14.6	23.2	--
0179	3.8 (est)	6.7	9.6	--	--
0245	2.6	10.5	--	--	--
Av.	4.0 ±1.0	9.1 ±1.6	12.1 ±2.5	23.2	15.6 ±3.4
<u>Compatible</u>					
0094 (platinum)	3.2	6.1	8.7	14.5	
0108 (6061-T6 aluminum with Apiezon-L)	0.7	9.8	13.4	21.4	
0133 (6061-T6 aluminum, brazed joint)	1.8	7.6	12.7	17.8	
0155 (EPR)	1.8	7.0	10.1	16.3	
<u>Noncompatible</u>					
0105 (6061-T6 aluminum with Rulon)	1.7	12.2	18.4	33.6	
0107 (6Al-4V titanium + Apiezon-L)	1.8	15.7	23.6	37.4	
0181 (6Al-4V titanium + EPR bonded)	12.1	17.7	27.0	--	
0243 (356-T6 aluminum)	3.0	11.5	--	--	
0244 ² (356-T6 aluminum)	0	4.7	--	--	

¹ Extrapolated from vapor pressure envelope of decomposition curve; 1-yr actual point is in doubt because of accelerated decomposition.

² Entered in noncompatible list because final fuel analysis is in close agreement with control sample and duplicate; although not detected, gage may have been in error.

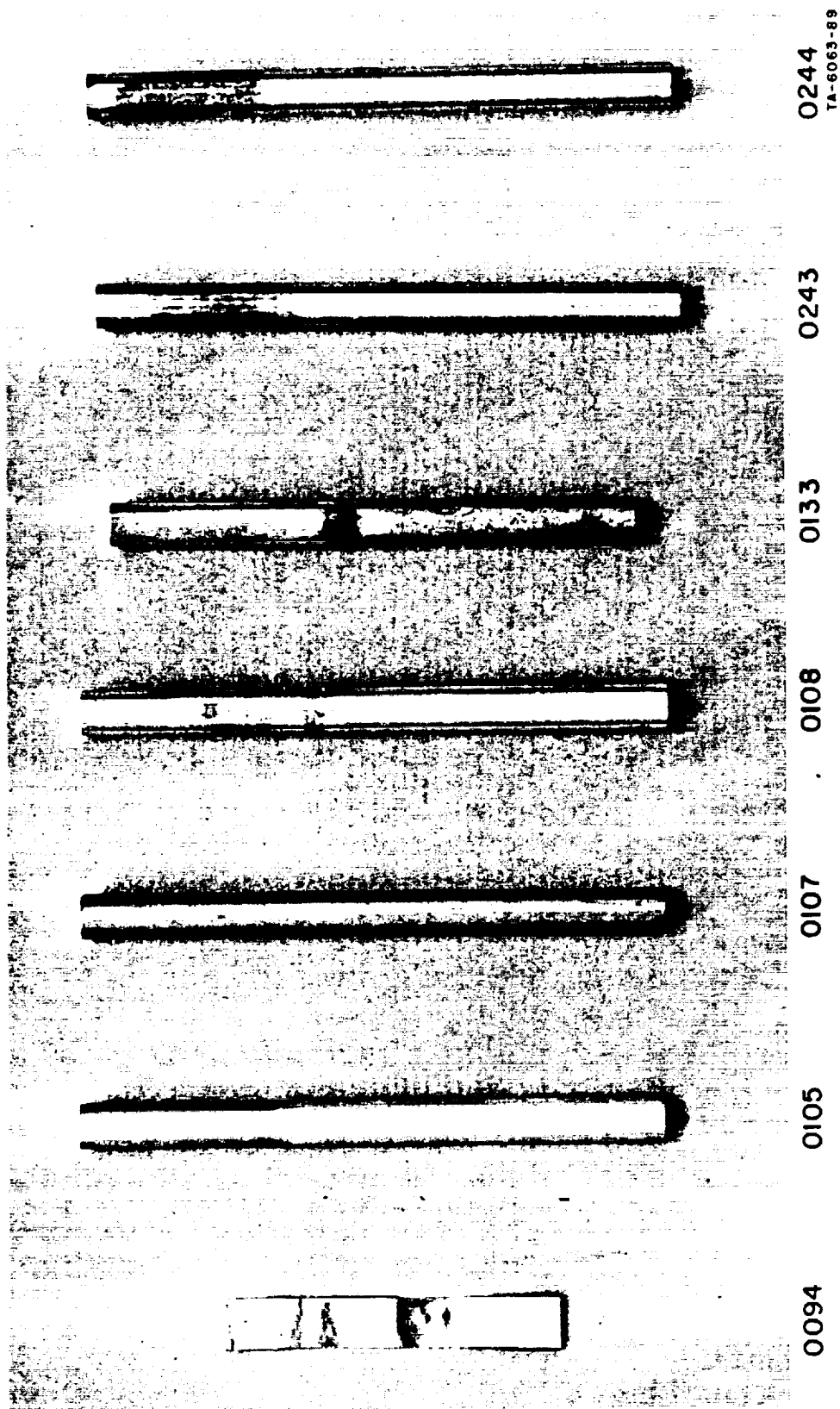
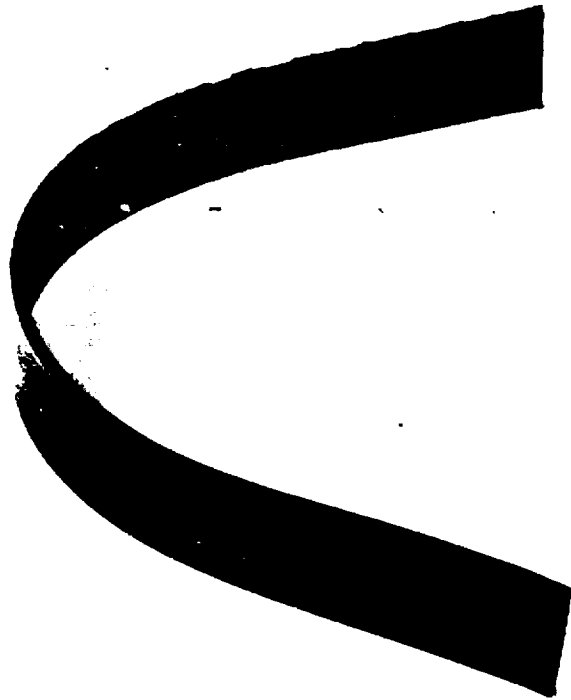


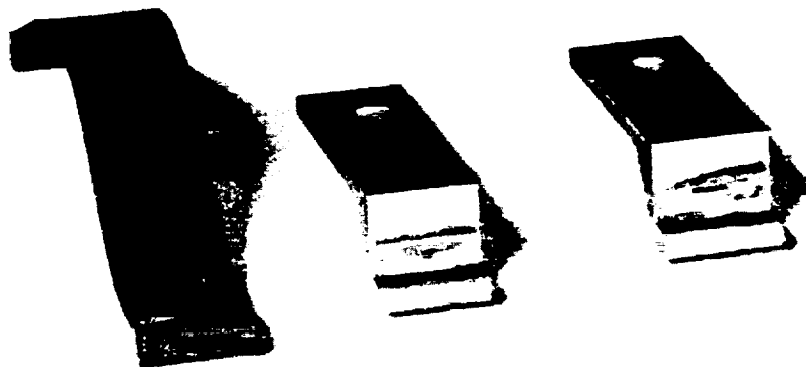
FIG. 11 APPEARANCE OF SPECIMENS AFTER STORAGE; TEST NOS. 0094 TO 0244

NOT REPRODUCIBLE



TA-6063-90

FIG. 12 APPEARANCE OF SPECIMENS AFTER STORAGE; TEST NO. 0155



TA-6063-91

FIG. 13 APPEARANCE OF SPECIMENS AFTER STORAGE; TEST NO. 0181

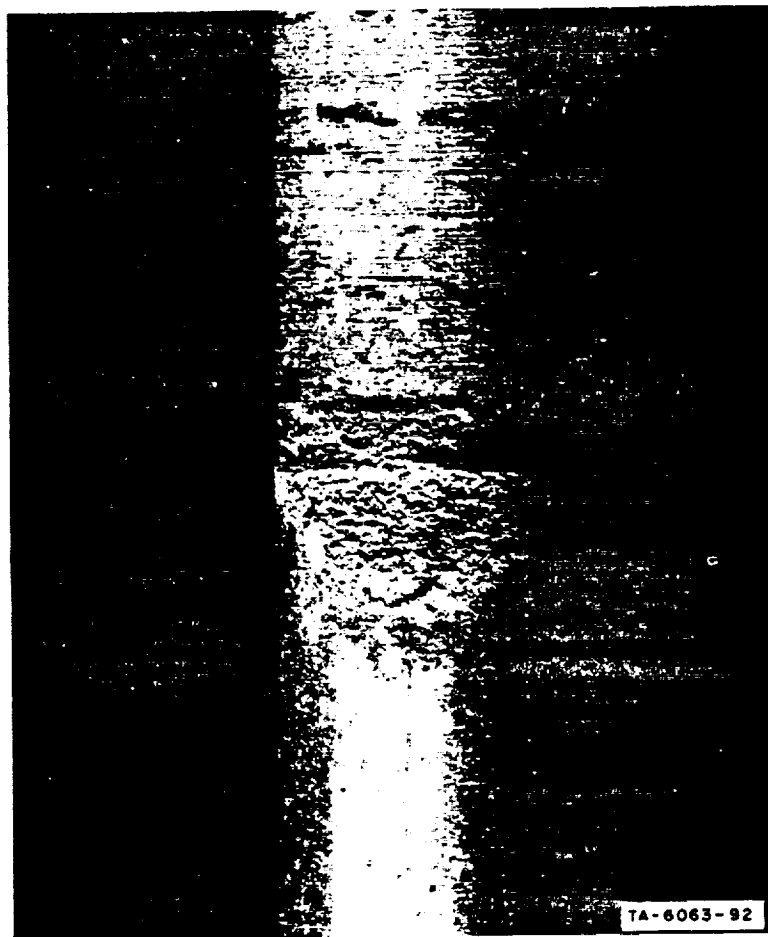


FIG. 14 APPEARANCE OF SPECIMEN NO. 0133; 10X ENLARGEMENT OF PHOTOMICROGRAPH

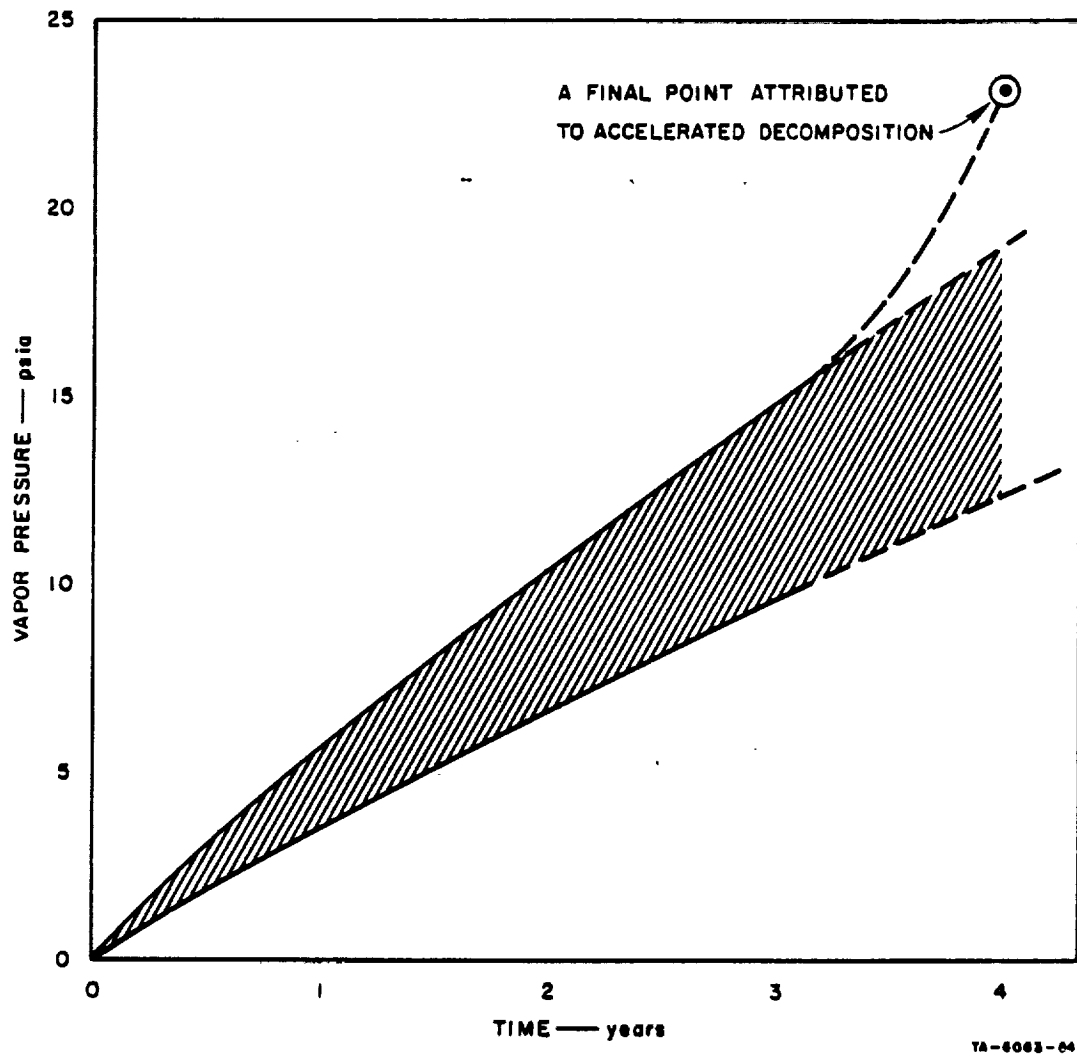


FIG. 15 VAPOR PRESSURE ENVELOPE OF THE DECOMPOSITION FOR THREE N_2H_4 CONTROL SAMPLES

V. RESULTS OF STORAGE TESTS WITH HYDRAZINE-HYDRAZINE NITRATE

The specimens in storage with hydrazine-hydrazine nitrate mixtures consisted of 6061-T6 aluminum alloy and various titanium alloys, stored individually and in loose combination. In general, 6061-T6 aluminum alloy appears to be compatible with hydrazine-hydrazine nitrate but compatibility and corrosion is variable when it is stored with the titanium alloys. Titanium alloys 6Al-4V (ELI), 5Al-2.5Sn (ELI), 6Al-6V-2Sn (HT), and 6Al-6V-2Sn are compatible with hydrazine-hydrazine nitrate, and 6Al-4V (ELI), 6Al-4V, and 6Al-6V-2Sn (annealed) apparently are compatible in combination with 6061-T6 aluminum. A great number of the stored specimens of both alloy groups indicate some corrosion such as etching and pitting; unfortunately, many of these already were spotted or stained before storage. A summary of corrosion rates and compatibilities is given in Table 10.

The analyses of the specimens are given in Table 11 and their appearance as received is shown photographically in Figs. 16 to 19. Photomicrographs of the ends of a number of the specimens are given in Figs. 20 to 23 and an enlarged photomicrograph of the 6061-T6 brazed joint in Fig. 24. The analysis of control hydrazine-hydrazine nitrate mixtures is given in Table 12 and of the mixtures stored with specimens in Table 13. Data on the ullage gases are summarized in Table 14 and normalized pressure data in Table 15.

The storage pressures of the control samples fall within the decomposition limits established for hydrazine itself (Fig. 15) except for a pair of short-term controls set up two years later (Table 15); the latter failure is attributed to some mishap or careless handling in assembly for storage since a concurrent test with 6061-T6 aluminum, generally compatible, is also outside of the normal decomposition curve.

Because of concern for the effect the metallic fittings and gages may have on the decomposition of the fuel, four concurrent control samples were stored in all-glass sealed systems. Of course, pressure data are not available for these samples, but no significant differences in ammonia content are observed (Table 12), indicating that the gage metals had little effect on decomposition.

The 6061-T6 aluminum alloy shows good compatibility stored by itself after acid passivation (0043) but not after a sodium hydroxide treatment (0042) whereupon it also incurs corrosive pitting. A short-term test (0237) indicates little corrosion but gross incompatibility; however, the conditions of storage assembly are suspect as described above for the control fuels (0239 and 0241). Stored with a brazed joint, 6061-T6 is not compatible even though corrosion is not evident; it is possible that the brazing flux was not removed completely prior to storage or that the braze metal is reactive with hydrazine nitrate whereas it was passive in the hydrazine alone (0133). Alternatively, it is possible that the increase in pressure was due to inadvertent introduction of extraneous impurities, for this sample had one of the largest amounts of water in the test series. These impurities might have had the same effect on decomposition as ascribed to the impurities introduced into the Rulon-coated sample in hydrazine (0105); this is also quite likely since the brazed joint was compatible in hydrazine alone.

The titanium alloys, whether stored singly or with 6061-T6 aluminum incurred corrosion rates of less than 1μ in/yr; however, staining, light pitting or etching, and light deposits were observed for the majority. The most poorly-prepared set of specimens (0222) indicated the most corrosion in a fuel with the largest water content, yet is apparently compatible as indicated by the pressure data and confirmed by the ammonia content of the propellant systems.

Positive conclusions as to the compatibility of 6061-T6 stored with the various titanium alloys cannot be made since all these 6061-T6 specimens were spotted before storage; thus, ratings are made only for

the tests examined and are not necessarily indicative of behavior in clean systems. For example, the unfortunate results for 6061-T6 and its control fuels after 2.4 years of storage (0237, 0239, 0241) are not credible in the light of other data. However, all these data might be quite applicable to actual flight conditions unless rigid control of cleanliness and fuel composition is undertaken.

Table 10

RESULTS OF JPL STORAGE TESTS: CORROSION RATES AND COMPATIBILITIES
WITH HYDRAZINE-HYDRAZINE NITRATE MIXTURE

JPL TEST NO.	MATERIAL	STORAGE TIME, yr	CORROSION		COMPATIBILITY ^f			
			μ in/yr	Rating ^a	1 Yr	2 Yr	2.6 Yr	4 Yr
0042	6061-T6 aluminum	4.25	0.7	3 ^b	NC	NC	NC	NC
0043	6061-T6 aluminum	4.25	0.5	1	C	C	C	C
0139	6061-T6 aluminum, brazed joint	3.9	<0.1	1	NC	NC	NC	NC
0209	6Al-4V titanium-ELI	2.6	0.4	1	C	C	C	--
0210	1) 6Al-4V titanium-ELI	2.6	0.7	1	C	C	C	--
	2) 6061-T6 aluminum	2.6	1.6	2 ^c				
0212	6Al-4V titanium	2.6	<0.1	1	C	NC	NC	--
0213	1) 6Al-4V titanium	2.6	<0.1	1	C	C	C	--
	2) 6061-T6 aluminum	2.9	<0.1	1 ^c				
0215	5Al-2.5 Sn titanium	2.6	<0.1	3	NC	NC	NC	--
0216	1) 5Al-2.5 Sn titanium	2.6	<0.1	1 ^c	NC	NC	NC	--
	2) 6061-T6 aluminum	2.6	1.6	3 ^c				
0218	5Al-2.5 Sn titanium-ELI	2.6	0.7	1	C	C	C	--
0219	1) 5Al-2.5 Sn titanium-ELI	2.6	<0.1	1	C	NC	NC	--
	2) 6061-T6 aluminum	2.6	0.4	3 ^c				
0221	6Al-6V-2 Sn titanium ^d	2.6	<0.1	1	C	C	C	--
0222	6Al-6V-2 Sn titanium ^d	2.6	0.6	3 ^c	C	C	C	--
	2) 6061-T6 aluminum	2.6	1.2	3 ^c				
0224	6Al-6V-2 Sn titanium ^e	2.6	<1.0	<1	C	C	C	--
0225	1) 6Al-6V-2 Sn titanium ^e	2.6	<0.1	3	NC	NC	NC	--
	2) 6061-T6 aluminum	2.6	2.8	3 ^c				
0237	6061-T6 aluminum	2.4	<0.1	1	NC	NC	NC	--

- a) 1 = excellent, <1 μ in/yr; attack limited to stain or extremely thin coating.
 2 = good, 1-3 μ in/yr; attack limited to stain or thin coating; no apparent etching or pitting.
 3 = not recommended, >1 μ in/yr; visible coating and flaking; apparent etching and/or pitting.

b) Pitting may be due to passivation treatment (NaOH).

c) Specimen in poor condition before storage.

d) Annealed.

e) HT-treated to 160,000 psi.

f) C = Compatible; within limits of decomposition rate of hydrazine.
 NC = Noncompatible; outside limits of decomposition rate of hydrazine.

Table 11
CORROSION OF TITANIUM AND ALUMINUM ALLOYS STORED
WITH HYDRAZINE-HYDRAZINE NITRATE MIXTURE

JPL TEST NO.	MATERIAL	WEIGHT CHANGE, g	DEPTH OF IMMERSION	APPEARANCE
0042	6061-T6 aluminum	-0.0003	total	many small pits over entire surface (may be due to passivation with NaOH); light yellow stain over all surfaces
0043	6061-T6 aluminum	-0.0002	total	no pit or etch; thin, colorless deposit over about 1/4 of surface
0139	6061-T6 aluminum, brazed joint	+0.0003	2/3	flux etch only; no etch at joint or interface, black stain at joint (immersed)
0209	6Al-4V titanium-ELI	-0.0002	2/3	stain and deposit at interface
0210	1) 6Al-4V titanium-ELI	-0.0003	2/3	brown stain at interface
0210	2) 6061-T6 aluminum ^a	-0.0004	2/3	no etch or pit; brown stain at interface; few light spots in vapor phase
0212	6Al-4V titanium	±0.0000	2/3	stain at interface, lengthwise fabrication marks
0213	1) 6Al-4V titanium	±0.0000	2/3	lengthwise fabrication marks
0213	2) 6061-T6 aluminum ^a	±0.0000	2/3	small, brown spotty stain over all
0215	5Al-2.5Sn titanium	±0.0000	2/3	pronounced intercrystalline etching, mostly in vapor phase
0216	1) 5Al-2.5Sn titanium	±0.0000	2/3	thin, white spotty deposit at interface
0216	2) 6061-T6 aluminum ^a	-0.0004	2/3	small scattered pits, light brown spots over all
0218	5Al-2.5Sn titanium-ELI	-0.0003	2/3	light stain at interface, some spots in vapor phase
0219	1) 5Al-2.5Sn titanium-ELI	+0.0001	2/3	no corrosion, stain, or deposit
0219	2) 6061-T6 aluminum ^a	-0.0001	2/3	light over-all pitting, brown spots over all
0221	6Al-6V-2Sn titanium ^b	+0.0001	2/3	light stain at interface
0222	1) 6Al-6V-2Sn titanium ^{b, c}	+0.0003	2/3	irregular pits on ends only; spotty white deposit on side, more at interface
0222	2) 6061-T6 aluminum ^a	-0.0003	2/3	fine pits over all, deposit at interface, thin white deposit in vapor phase
0224	6Al-6V-2Sn titanium ^d	+0.0001	2/3	thin deposit at interface
0225	1) 6Al-6V-2Sn titanium ^d	±0.0000	2/3	localized pits on end in vapor phase; light stain at interface
0225	2) 6061-T6 aluminum ^a	-0.0007	2/3	many small pits in liquid phase; stain and deposit in vapor phase
0237	6061-T6 aluminum	+0.0002	9/10	deposit on both ends, nothing on side or at interface

a) Records show specimens were spotted before storage.

b) Annealed.

c) Records show that paint was on both ends of specimen before storage.

d) HT-treated to 160,000 psi.

Table 12

ANALYSIS OF HYDRAZINE-HYDRAZINE NITRATE CONTROL SAMPLES

JPL TEST NO.	STORAGE TIME, yr	FUEL WT., g	COMPOSITION, WT-%					RESIDUE, WT-% AT 500°C
			N ₂ H ₄	HNO ₃	C ₆ H ₅ NH ₂	H ₂ O	NH ₃	
0151	3.75	21.7	81.4	15.5	0.36	1.38	0.73	0.005
0151 ^a	3.75	21.9	81.4	15.3	0.36	1.58	0.61	0.004
0152	3.75	21.5	81.4	15.6	0.35	1.51	0.50	0.002
0152 ^a	3.75	22.5	81.5	15.6	0.43	1.47	0.43	0.002
0153	3.75	22.5	81.0	15.8	0.36	1.68	0.78	0.005
0153 ^{a, b}	3.75	23.0	81.4	15.4	0.35	1.60	0.88	0.001
0154	3.75	22.4	81.6	15.0	0.39	2.08	0.53	0.004
0154 ^a	3.75	22.2	81.4	15.4	0.36	1.49	0.69	0.002
0239 ^c	2.4	30.0	81.8	15.6	0.38	1.20	0.90	0.002
0241 ^c	2.4	28.9	81.6	15.0	0.32	1.28	1.18	0.001

a) Test capsule was all glass, no gage or metal fittings.

b) JPL record notes possible leak.

c) Control for #0237; reference for #0209.0225.

Table 13
ANALYSIS OF HYDRAZINE-HYDRAZINE NITRATE MIXTURE STORED
WITH TITANIUM AND ALUMINUM ALLOYS

JPL TEST NO.	MATERIAL	STORAGE TIME, yr	FUEL WT., g	COMPOSITION, WT-%					RESIDUE, WT-% AT 500°C
				N ₂ H ₄	HNO ₃	C ₆ H ₅ NH ₂	H ₂ O	NH ₃	
0042	6061-T6 aluminum	4.25	42.8	81.02	15.3	0.42	1.60	0.98	0.005
0043	6061-T6 aluminum	4.25		(capsule broken in handling)					
0139	6061-T6 aluminum, brazed joint	3.9	20.2	80.84	15.2	0.42	2.17	0.84	0.006
0209	1) 6Al-4V titanium-ELI	2.6	21.7	81.96	15.2	0.34	1.10	0.77	0.0002
0210	1) 6Al-4V titanium-ELI 2) 6061-T6 aluminum	2.6	21.2	81.82	15.5	0.36	1.21	0.50	0.002
0212	6Al-4V titanium	2.6	22.0	81.77	15.4	0.32	1.27	0.70	0.004
0213	1) 6Al-4V titanium 2) 6061-T6 aluminum	2.6	20.3	81.84	15.2	0.31	1.09	0.49	0.001
0215	5Al-2.5Sn titanium	2.6	20.0	81.50	15.5	0.32	1.33	0.83	0.001
0216	1) 5Al-2.5Sn titanium 2) 6061-T6 aluminum	2.6	20.6	81.63	15.5	0.36	1.35	1.58	0.001
0218	5Al-2.5Sn titanium-ELI	2.6	20.1	81.85	15.3	0.32	1.33	0.53	<0.001
0219	1) 5Al-2.5Sn titanium-ELI 2) 6061-T6 aluminum	2.6	21.6	81.27	15.5	0.33	1.23	0.69	0.002
0221	6Al-6V-2Sn titanium ^a	2.6	20.6	81.90	15.2	0.37	1.07	0.87	<0.001
0222	1) 6Al-6V-2Sn titanium ^a 2) 6061-T6 aluminum	2.6	21.9	81.62	15.4	0.37	2.66	0.40	0.001
0224	6Al-6V-2Sn titanium ^b	2.6	22.2	81.97	15.2	0.34	0.92	0.80	0.003
0225	1) 6Al-6V-2Sn titanium ^b	2.6		(capsule broken when received)					
0237	6061-T6 aluminum	2.4	30.0	81.67	15.4	0.34	1.15	0.80	0.001

a) Annealed.

b) HT-treated to 160,000 psi.

Table 14
ANALYSIS OF ULLAGE GASES OVER HYDRAZINE-HYDRAZINE NITRATE MIXTURE
STORED WITH TITANIUM AND ALUMINUM ALLOYS

JPL TEST NO.	MATERIAL	STORAGE TIME, yr	ULLAGE VOLUME, cc	FINAL PRESSURE AT 110°F, psia	PRESSURE AFTER STORAGE, psia			NONCONDENSABLE GASES, mol- ratio N ₂ /H ₂	O ₂ CONSUMED, mol-ratio O ₂ /H ₂
					22°C	-25°C	-195°C		
0042	6061-T6 aluminum	4.25	34	38.0	32.0	23.0	8.8	17.9	1.22
0043 ^a	6061-T6 aluminum	4.25	35	21.0	--	12.0	--	--	--
0139	6061-T6 aluminum brazed joint	3.9	57	19.5	14.9	10.0	2.1	14.72	0.33
0151	Control	3.75	58	10.0	9.0	7.0	1.2	9.01	1.07
0151 ^a	Control, no gage	3.75	54	--	--	--	--	5.50	10.8
0152	Control	3.75	59	6.0	3.5	1.0	0.0	--	--
0152 ^a	Control, no gage	3.75	54	--	--	--	--	--	--
0153	Control	3.75	60	14.5	10.7	7.0	1.4	7.70	0.76
0153 ^{a,b}	Control; no gage	3.75	52	--	--	--	--	1.75	13.0
0154	Control	3.75	59	6.0	2.8	0.0	0.0	--	--
0154 ^a	Control, no gage	3.75	53	--	--	--	--	--	--
0209	6Al-4V titanium-ELI	2.6	55	9.0	5.5	4.0	0.0	--	--
0210	1) 6Al-4V titanium-ELI 2) 6061-T6 aluminum	2.6	53	10.0	6.3	4.5	0.0	--	--
0212	6Al-4V titanium	2.6	56	16.0	11.7	8.5	2.3	18.87	1.07
0213	1) 6Al-4V titanium 2) 6061-T6 aluminum	2.6	55	10.0	7.4	5.0	0.0	--	--
0215	5Al-2.5Sn titanium	2.6	55	27.5	21.0	16.0	6.0	9.00	0.24
0216	1) 5Al-2.5Sn titanium 2) 6061-T6 aluminum	2.6	54	36.0	29.0	21.0	8.0	8.13	0.23
0218	5Al-2.5Sn titanium-ELI	2.6	57	8.0	5.5	2.5	0.0	--	--
0219	1) 5Al-2.5Sn titanium-ELI 2) 6061-T6 aluminum	2.6	55	19.5	14.7	10.5	2.8	15.43	0.84
0221	6Al-4V titanium (annealed)	2.6	55	11.0	7.3	5.5	1.8	13.07	2.24
0222 ^a	1) 6Al-4V titanium (annealed) 2) 6061-T6 aluminum	2.6	57	5.5	2.8	2.0	2.0	5.79	3.72
0224	6Al-6V-2Sn titanium (HT)	2.6	57	11.0	7.5	5.0	0.0	--	--
0225 ^c	1) 6Al-6V-2Sn titanium (HT) 2) 6061-T6 aluminum	2.6	--	13.0	--	--	--	--	--
0237	6061-T6 aluminum	2.4	49	25.0	20.0	15.0	8.0	22.73	1.72
0239	Control	2.4	50	17.0	13.7	9.5	2.4	20.65	2.11
0241	Control	2.4	52	39.5	32.0	24.0	9.0	28.37	2.32

a) Capsule broken in handling.
b) Possible leak recorded by JPL.
c) Capsule broken in shipment.

Table 15

DECOMPOSITION OF HYDRAZINE-HYDRAZINE NITRATE MIXTURES AS CONTROL
 SAMPLES AND WITH STORED SPECIMENS (PRESSURE DATA)

JPL TEST NO.	SPECIMENS	PRESSURE (Normalized to 45-cc Ullage), psia			
		1 Yr	2 Yr	2.6 Yr	4 Yr
0151	Control	4.5	5.2	5.8	12.9
0152	Control	2.6	2.6	3.3	7.9
0153	Control	4.7	6.7	8.0	19.3
0154	Control	3.3	5.3	5.3	7.9
0239	Control	7.8	15.6	20.0	--
0241	Control	18.5	36.4	45.5	--
0042	6061-T6 Al	8.3	15.1	17.4	26.2
0043	6061-T6 Al	3.9	7.0	9.4	14.8
0139	6061-T6 Al, brazed	7.6	11.4	13.9	24.0
0209	6Al-4V Ti-ELI	4.9	8.6	11.0	--
0210	6Al-4V Ti-ELI with 6061-T6 Al	4.7	8.9	11.8	--
0212	6Al-4V Ti	5.6	13.7	19.3	--
0213	6Al-4V Ti with 6061-T6 Al	4.9	9.2	12.2	--
0215	5Al-2.5Sn Ti	9.8	23.2	33.5	--
0216	5Al-2.5Sn Ti with 6061-T6	15.6	31.2	19.0	--
0218	5Al-2.5Sn Ti-ELI	3.8	7.6	10.1	--
0219	5Al-2.5Sn Ti-ELI with 6061-T6	4.9	14.7	23.2	--
0221	6Al-6V-2Sn Ti (an'd)	3.1	9.8	12.9	--
0222	6Al-6V-2Sn Ti (an'd) with 6061-T6	2.5	5.1	7.6	--
0224	6Al-6V-2Sn Ti (HT)	2.5	9.5	13.3	--
0225	6Al-6V-2Sn Ti (HT) with 6061-T6	6.1	11.6	15.3	--
0237	6061-T6 Al	9.8	20.6	26.2	

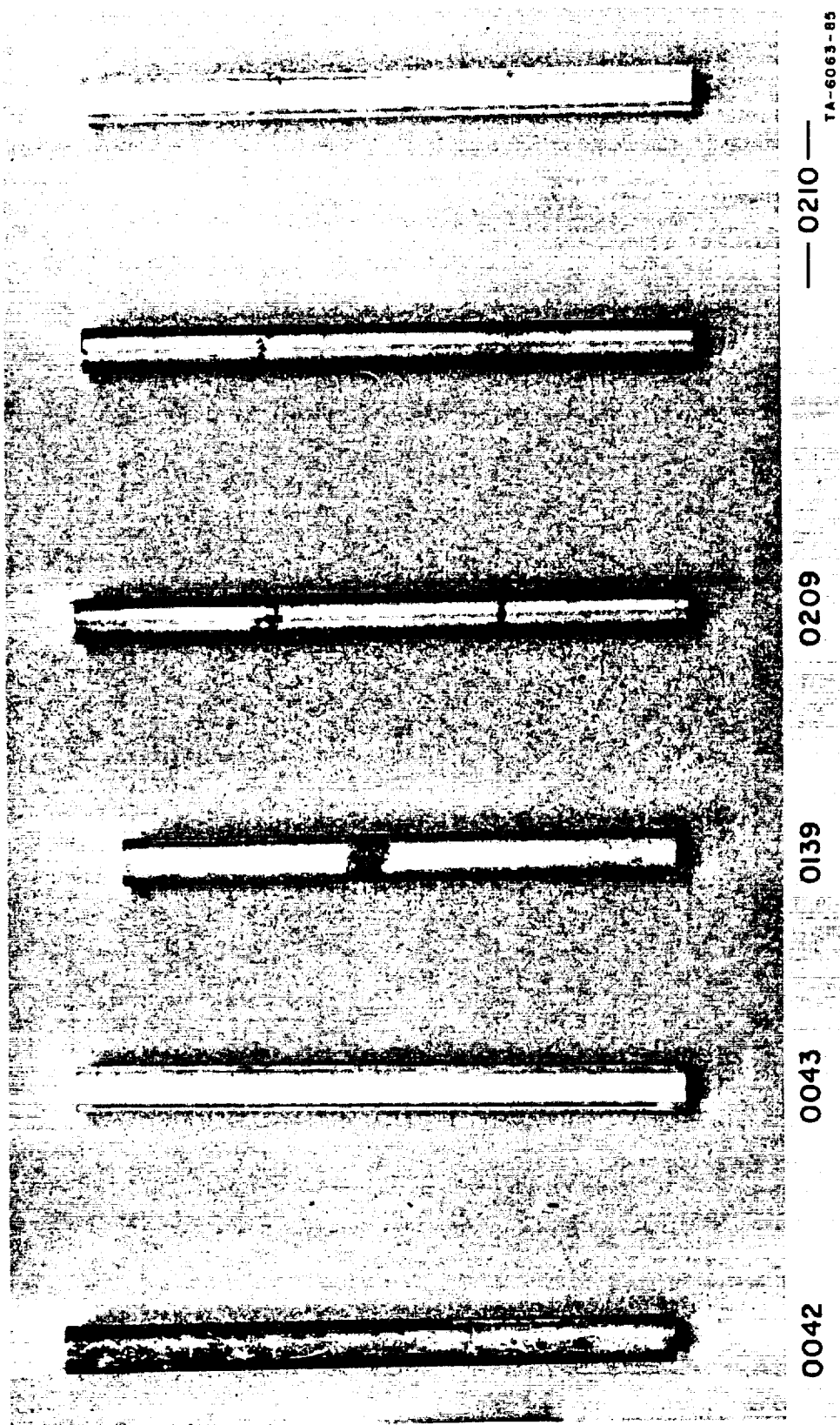


FIG. 16 APPEARANCE OF SPECIMENS AFTER STORAGE; TEST NOS. 0042 TO 0210

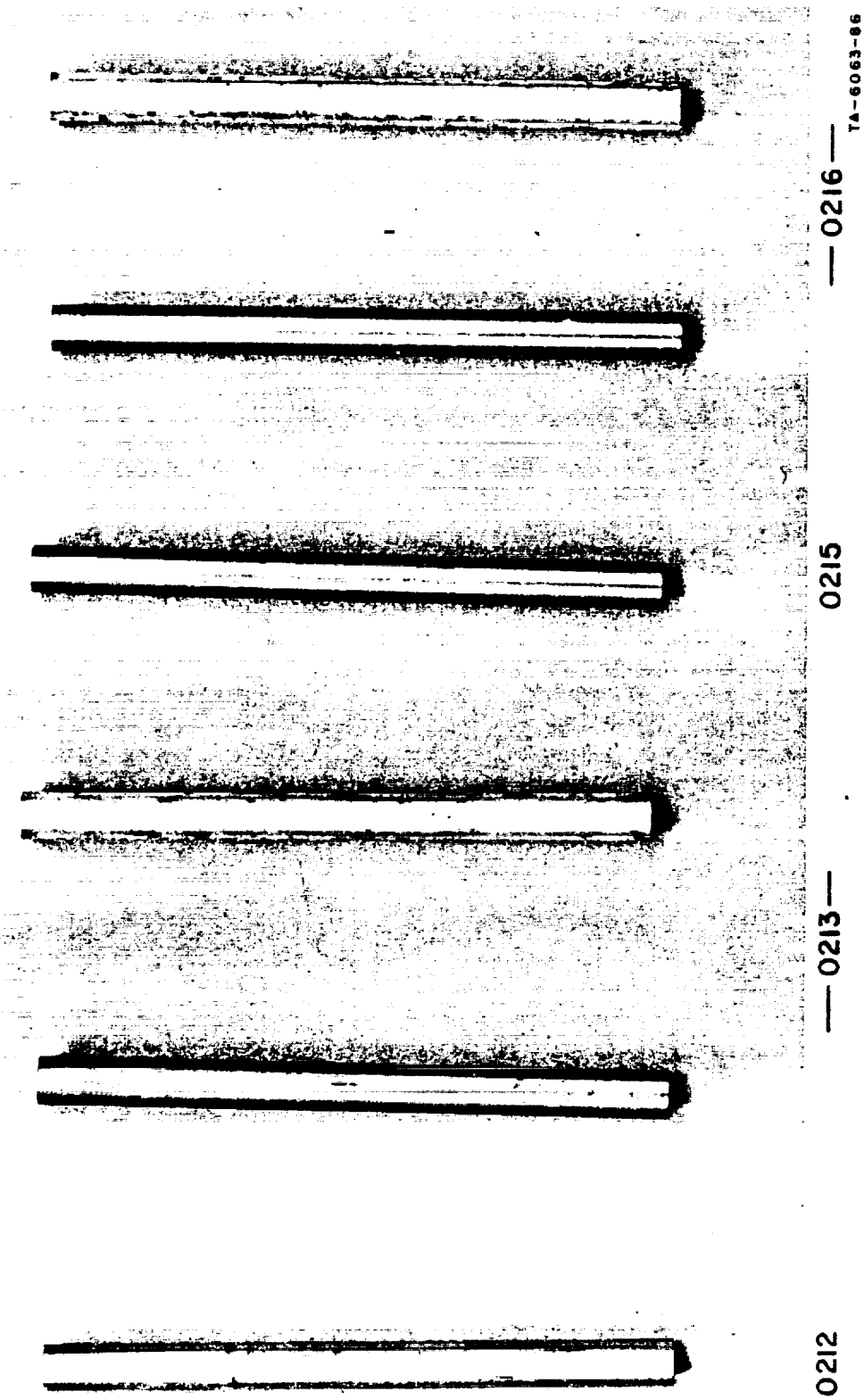


FIG. 17 APPEARANCE OF SPECIMENS AFTER STORAGE; TEST NOS. 0212 TO 0216

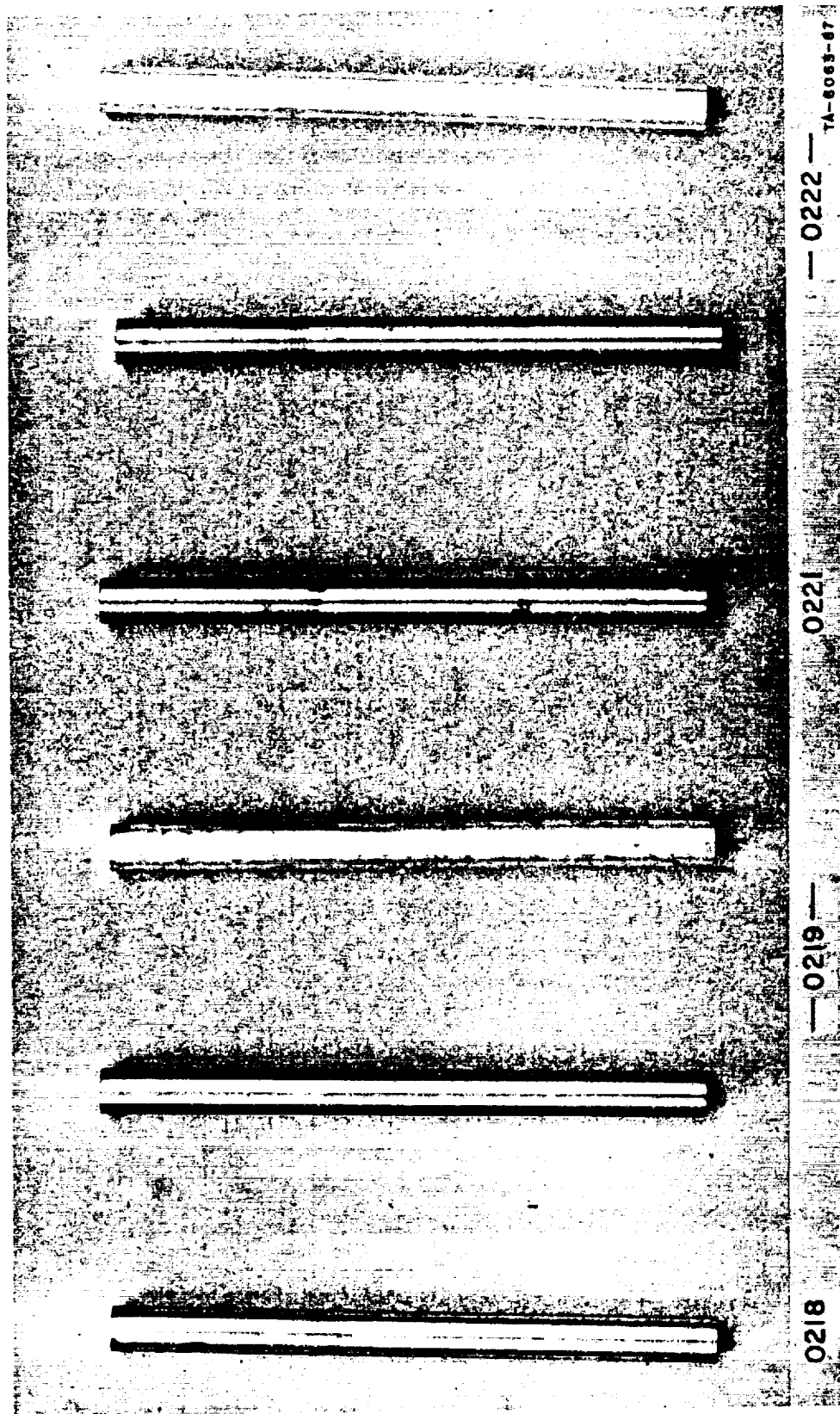


FIG. 18 APPEARANCE OF SPECIMENS AFTER STORAGE; TEST NOS. 0218 TO 0222

NOT REPRODUCIBLE

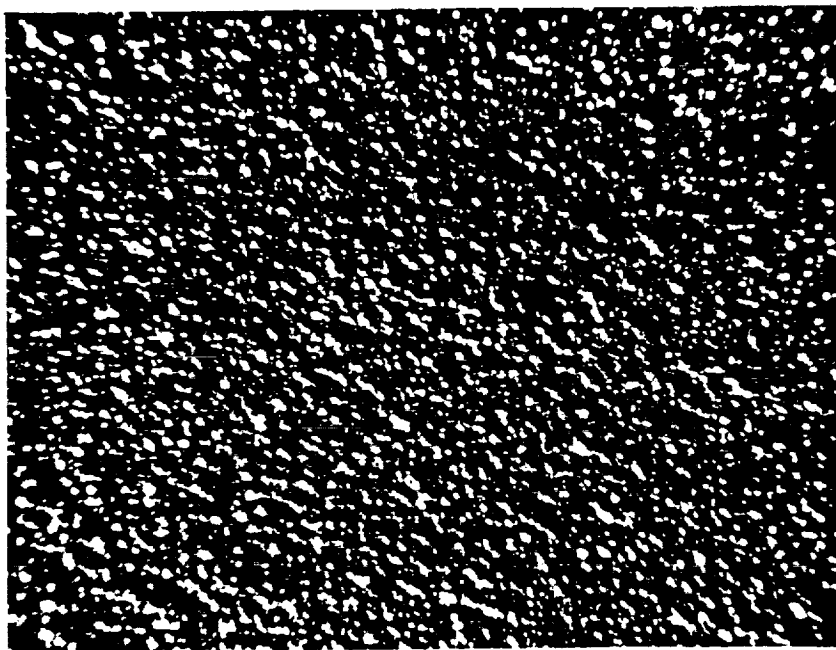
TA-6063-88

0227

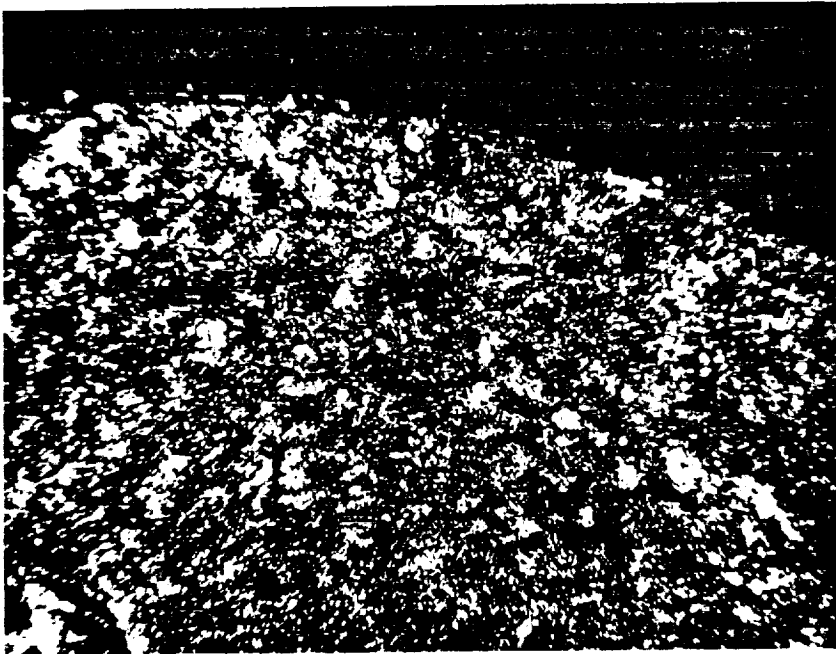
— 0225 —

0224

FIG. 19 APPEARANCE OF SPECIMENS AFTER STORAGE; TEST NOS. 0224 TO 0227



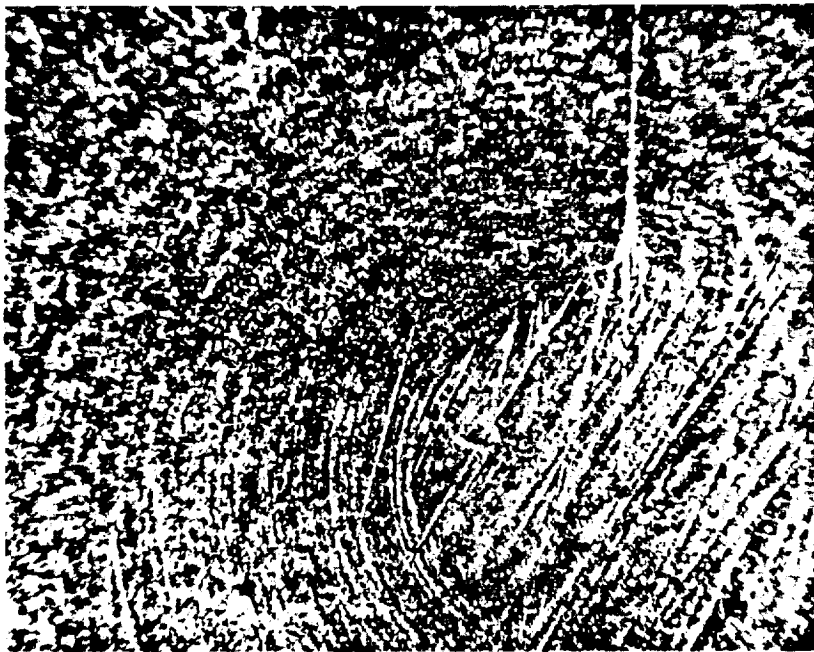
0042



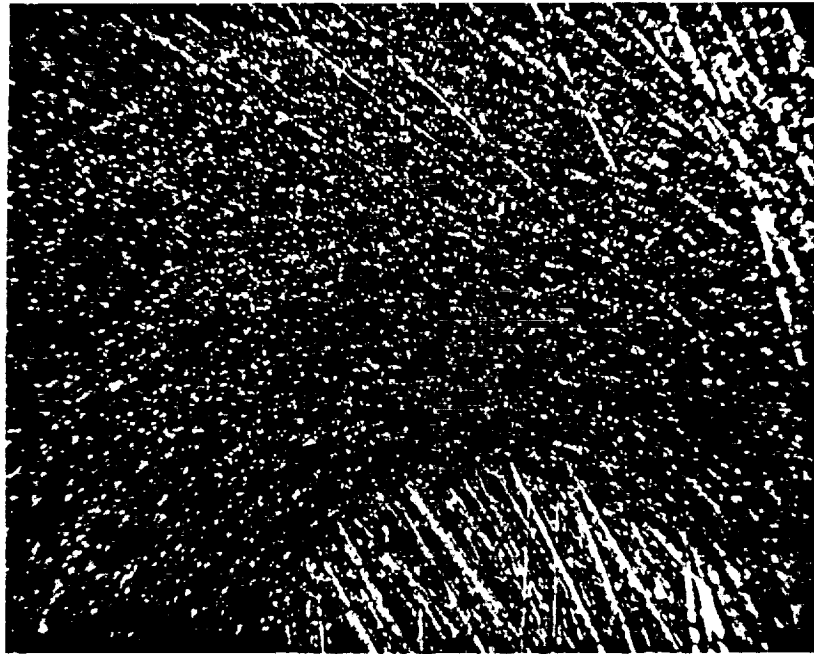
0215

TA-6063-93

FIG. 20 PHOTOMICROGRAPHS OF THE ENDS OF SPECIMENS AFTER STORAGE (60X): (0042) 6061-T6 ALUMINUM;
(0215) 5A1-2.5Sn TITANIUM



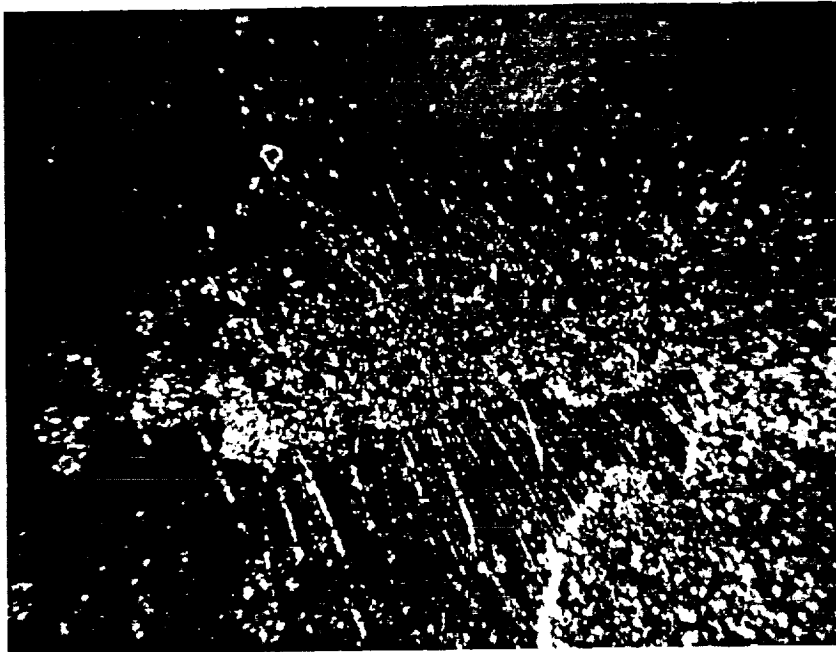
0216-2



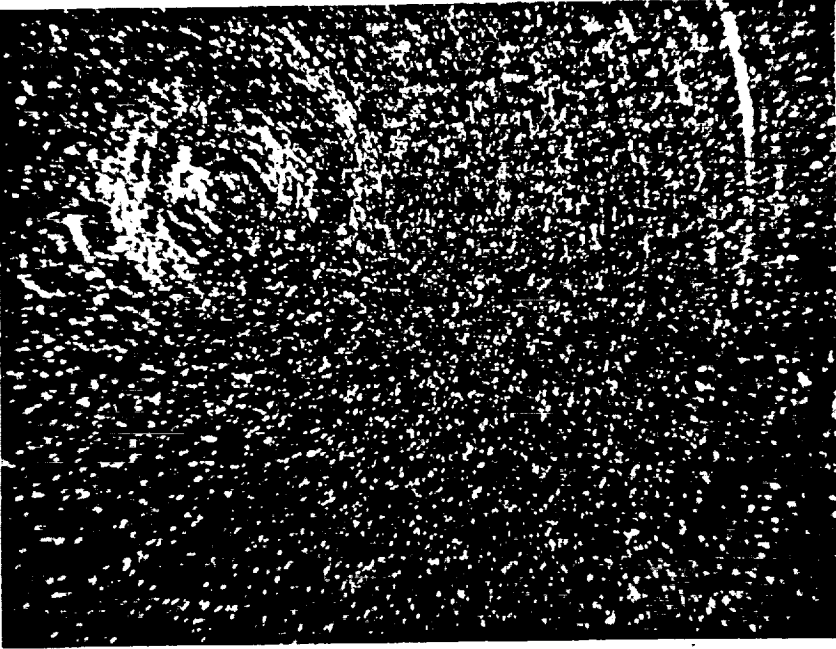
0219-2

TA-6063-94

FIG. 21 PHOTOMICROGRAPHS OF THE ENDS OF SPECIMENS AFTER STORAGE (60X): (0216-2) 6061-T6 ALUMINUM;
(0219-2) 6061-T6 ALUMINUM



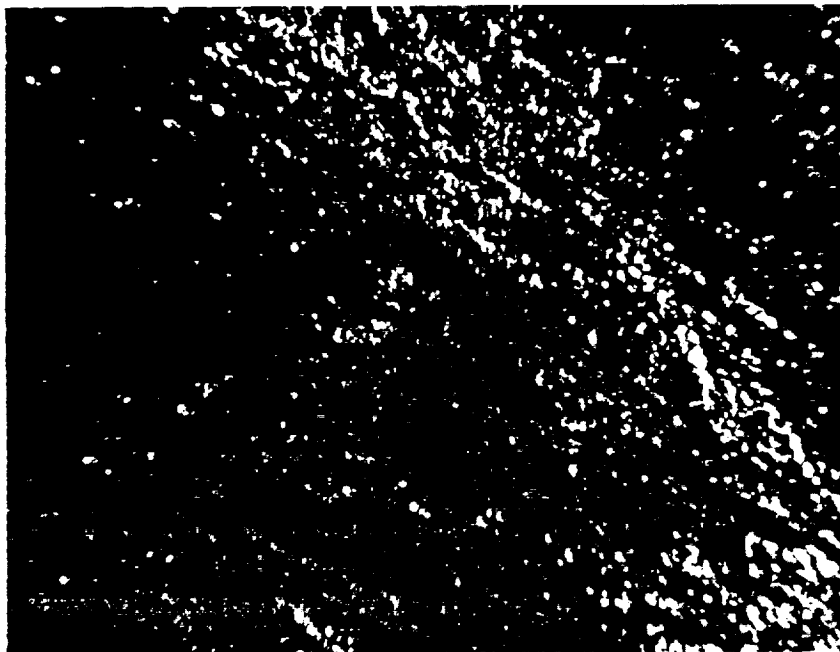
0222-1



0222-2

TA - 6063 - 95

FIG. 22 PHOTOMICROGRAPHS OF THE ENDS OF SPECIMENS AFTER STORAGE (60X): (0222-1) 6A1-6V-25n TITANIUM, ANNEALED; (0222-2) 6061-T6 ALUMINUM



0225-1



0225-2

TA-6063-96

FIG. 23 PHOTOMICROGRAPHS OF THE ENDS OF SPECIMENS AFTER STORAGE (60X): (0225-1) 6A1-6V-2Sn TITANIUM-HT (0225-2) 6061-T6 ALUMINUM

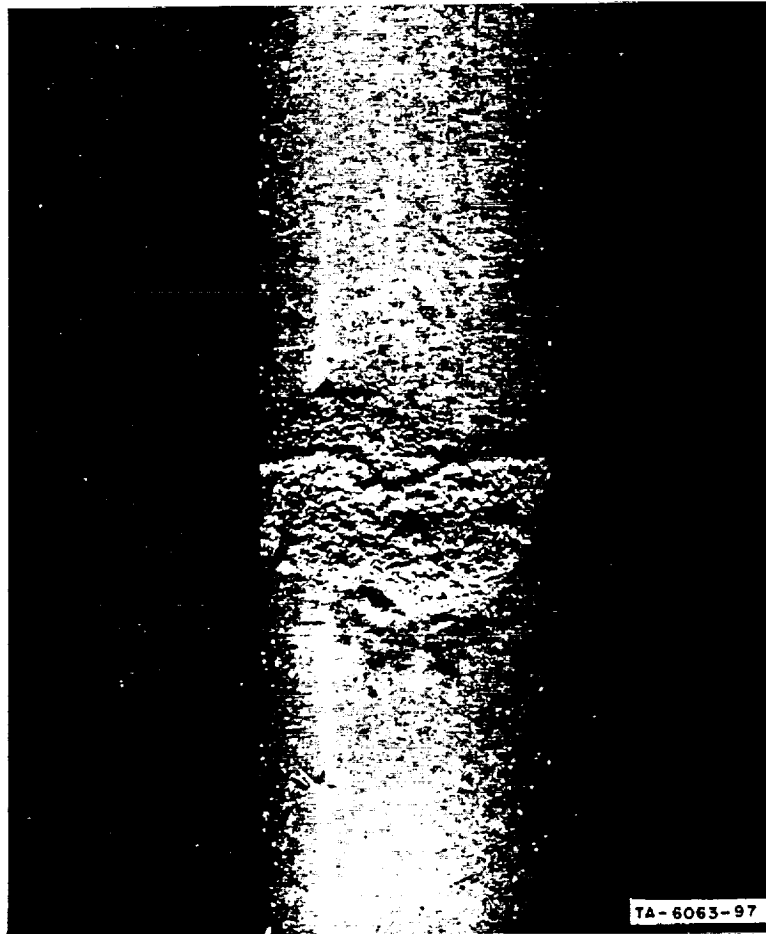


FIG. 24 BRAZED JOINT ON 6061-T6 ALUMINUM (10K)

VI. RESULTS OF STORAGE TESTS IN HYDRAZINE-UDMH

All of the specimens stored in the hydrazine-UDMH mixture were 6Al-4V titanium alloy and appear to be incompatible with the fuel. After 1 year of storage, normalized ullage pressures (at 45-cc volumes) exceeded the upper limits of the decomposition-rate curve (Figure 15) for hydrazine by 1 to 12 psia; after 1.8 years, three of the test pressures appeared to be within the limits but the remainder were excessive by 0.5 to 20 psia. It is interesting to note that the average pressure at the 1.8-year storage period of 13.9 psia closely approximates that of 16.7 psia at the 2-year period for the two 6Al-4V titanium alloys stored with hydrazine only (0107 and 0181). The terminal pressures of the two control samples were excessive by 2.3 and 18.8 psia (normalized). Since there is no way of estimating any fault in storage assembly procedures, and in view of generally excessive pressures, it seems appropriate to recommend that this alloy not be used with hydrazine-UDMH.

On the other hand, there was no evidence of corrosive attack on the specimens except for staining, and corrosion rates were at low levels of 0.6 to 2.1 $\mu\text{in/yr}$ (see Table 16). The appearance of these specimens as received is shown in Figures 25 and 26 and the analyses are summarized in Table 17. Analyses of the fuels and ullage gases are recorded in Tables 18 and 19, respectively, and the normalized ullage pressures are given in Table 20.

Two of the test gages were found faulty when opened to the atmosphere (0264 and 0273).

Table 16

RESULTS OF JPL STORAGE TESTS: CORROSION RATES
AND COMPATIBILITIES IN HYDRAZINE-UDMH

JPL TEST NO.	MATERIAL	STORAGE TIME, yr	CORROSION		COMPATIBILITY	
			μ in/yr	Rating ^a	1 Yr	1.8 Yr
0263	6Al-4V titanium	1.8	0.6	1	NC	NC
0264	6Al-4V titanium	1.8	0.6	1	-- ^c	-- ^c
0265	6Al-4V titanium	1.8	0.6	1	NC	NC
0266	6Al-4V titanium	1.8	0.8	1	NC	NC
0267	6Al-4V titanium	1.8	0.8	1	NC	C
0268	6Al-4V titanium	1.8	0.8	1	NC	NC
0269	6Al-4V titanium	1.8	0.6	1	NC	NC
0271	6Al-4V titanium	1.8	1.2	2	NC	NC
0272	6Al-4V titanium	1.8	0.6	1	NC	C
0273	6Al-4V titanium	1.8	2.1	2	-- ^c	-- ^c
0274	6Al-4V titanium	1.8	1.5	2	NC	NC

- a) 1 = excellent, $<1 \mu$ in/yr; attack limited to stain or extremely thin coating;
 2 = good, $1-3 \mu$ in/yr; attack limited to stain or thin coating; no apparent etching or pitting;
 3 = not recommended, $>1 \mu$ in/yr; visible coating and flaking; apparent etching and/or pitting.
- b) C = Compatible; within limits of hydrazine decomposition-rate curve.
 NC = Noncompatible; outside limits of hydrazine decomposition-rate curve.
- c) Faulty gages; no estimate made.

Table 17
CORROSION OF 6AL-4V TITANIUM ALLOY
STORED IN HYDRAZINE-UDMH

JPL TEST NO.	WEIGHT CHANGE, g	DEPTH OF IMMERSTION	APPEARANCE
0263	-0.0002	4/5	no indication of corrosion, no stain
0264	-0.0002	4/5	slight stain at interface, thin white deposit in spots in liquid phase
0265	-0.0002	4/5	slight stain at interface, thin de- posit in spots over all
0266	-0.0003	4/5	no indication of corrosion, no stain
0267	-0.0003	4/5	no corrosion or stain evident
0268	-0.0003	4/5	no corrosion or stain evident
0269	-0.0002	2/3	light stain at interface, no attack
0271	-0.0004	2/3	thin, white spotty deposit in liquid phase
0272	-0.0002	2/3	no corrosion or stain evident
0273	-0.0007	2/3	no corrosion or stain evident
0274	-0.0005	2/3	no corrosion or stain evident

Table 18

ANALYSIS OF HYDRAZINE-UDMH STORED
WITH 6AL-4V TITANIUM (AND CONTROLS)

JPL TEST NO.	STORAGE TIME, yr	FUEL WT., g	COMPOSITION WT-%				RESIDUE, WT-%	
			N ₂ H ₄	UDMH*	C ₆ H ₅ NH ₂	H ₂ O	at 100°C	at 500°C
0263	1.8	17.8	49.7	49.6	0.16	0.58	0.007	<0.001
0264	1.8	17.4	50.0	48.5	0.17	0.67	0.009	0.002
0265	1.8	18.0	50.5	48.5	0.16	0.74	0.006	0.001
0266	1.8	17.6	49.6	49.1	0.18	0.77	0.011	0.003
0267	1.8	18.1	50.2	48.5	0.16	0.58	0.006	0.001
0268	1.8	18.0	49.9	48.9	0.17	0.58	0.003	<0.001
0269	1.8	17.9	49.0	50.6	0.16	0.74	0.010	0.003
0271	1.8	18.0	50.1	49.7	0.16	0.60	0.005	0.002
0272	1.8	18.0	51.0	48.4	0.16	0.69	0.005	0.003
0273	1.8	17.7	50.0	49.6	0.18	0.63	0.007	0.003
0274	1.8	18.1	50.8	48.4	0.17	0.60	0.007	<0.001
CONTROLS								
0263A	1.8	16.7	49.8	48.4	0.19	0.66	0.009	0.001
0269A	1.8	17.8	48.7	50.9	0.20	0.96	0.007	<0.001

*UDMH values include ammonia content (see Section III).

Table 19

ANALYSIS OF ULLAGE GASES OVER HYDRAZINE-UDMH
STORED WITH 6AL-4V TITANIUM ALLOY

JPL TEST NO.	STORAGE TIME, yr	ULLAGE VOLUME, cc	FINAL PRESSURE AT 110°F, psia	PRESSURE AFTER STORAGE, psia			NONCONDENSABLE GASES, mol- ratio, N ₂ :H ₂	O ₂ CONSUMED, mol-ratio O ₂ :H ₂
				22°C	-25°C	-195°C		
0263A	1.8	42.8	12.5	7.8	4.5	0.0	--	--
0263	1.8	35.5	25.0	18.5	13.0	3.6	11.10	1.44
0264 ^a	1.8	38.5	7.5	3.3	0.0	0.0	--	--
0265	1.8	34.2	11.5	6.4	3.0	0.0	--	--
0266	1.8	32.3	15.5	10.5	7.0	1.0	10.38	2.12
0267	1.8	39.2	10.0	6.0	1.5	0.0	--	--
0268	1.8	39.0	15.0	10.5	6.0	1.0	5.59	0.70
0269	1.8	48.5	13.0	9.2	5.5	1.0	10.36	2.50
0269A	1.8	38.2	33.5	28.5	19.0	5.5	19.59	3.35
0271	1.8	57.8	23.0	17.0	11.5	3.6	24.43	1.68
0272	1.8	54.1	8.0	3.7	1.0	0.0	--	--
0273 ^b	1.8	32.0	16.5	11.2	7.5	1.4	8.31	1.00
0274	1.8	53.7	8.5	4.2	1.6	0.0	--	--

a) Gage opened to atmosphere reads 11.6 psia at 25°C.

b) Gage opened to atmosphere reads 13.8 psia at 25°C.

Table 20

DECOMPOSITION OF HYDRAZINE-UDMH
AS CONTROL SAMPLES AND WITH
6AL-4V TITANIUM ALLOY
(Pressure Data)

JPL TEST NO:	PRESSURE (Normalized to 45-cc Volume), psia		
	6 mos.	1 Yr	1.8 Yr
Controls			
0263A	3.8	8.1	11.9
0269A	5.5	12.3	28.4
Specimens			
0263	3.2	9.5	19.7
0265	3.8	6.5	8.7
0266	4.3	7.9	11.1
0267	3.3	10.2	8.7
0268	3.5	7.8	13.0
0269	3.2	8.6	14.0
0271	4.3	17.8	29.8
0272	3.6	7.8	9.6
0274	5.9	11.3	10.1

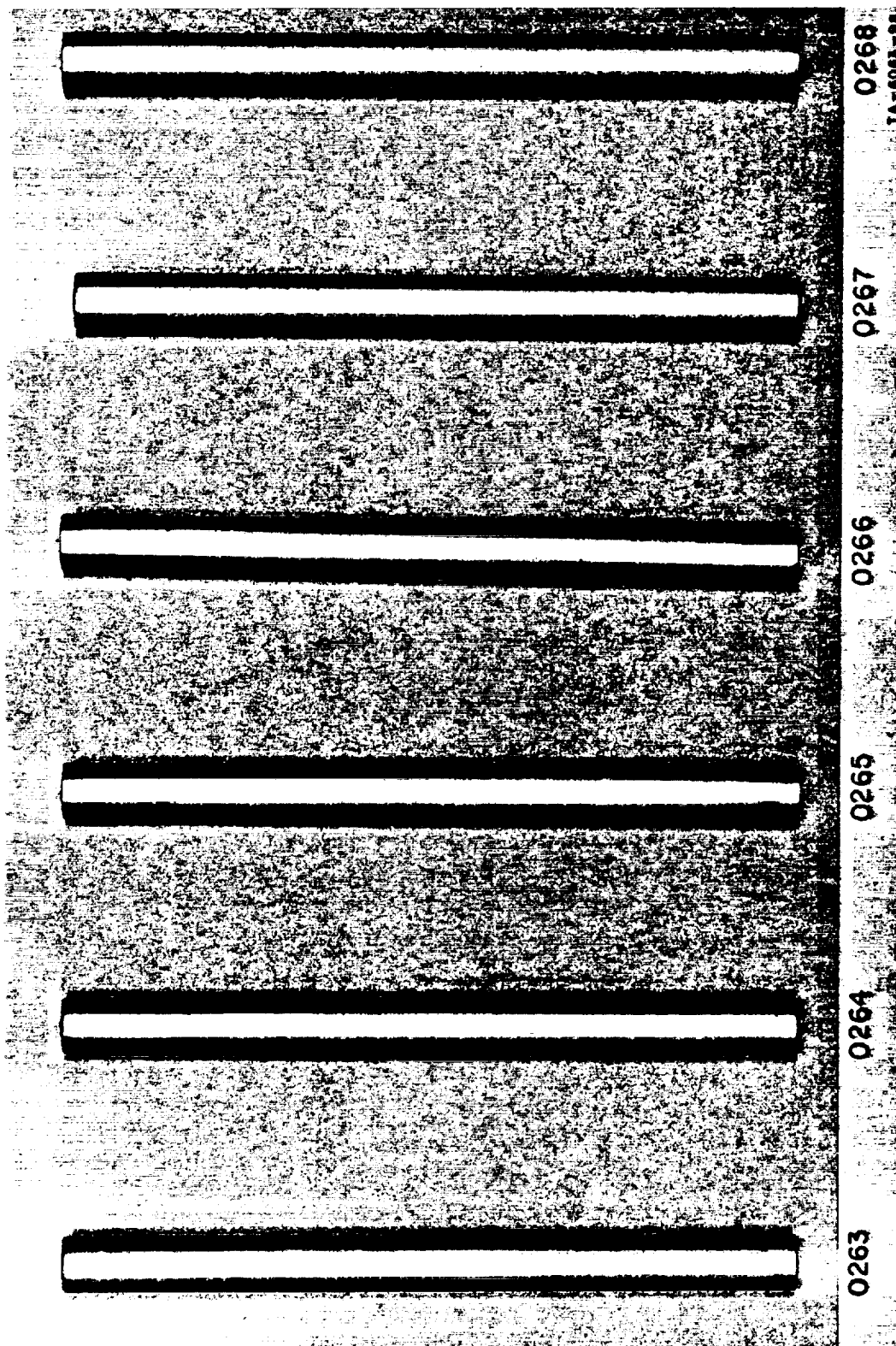
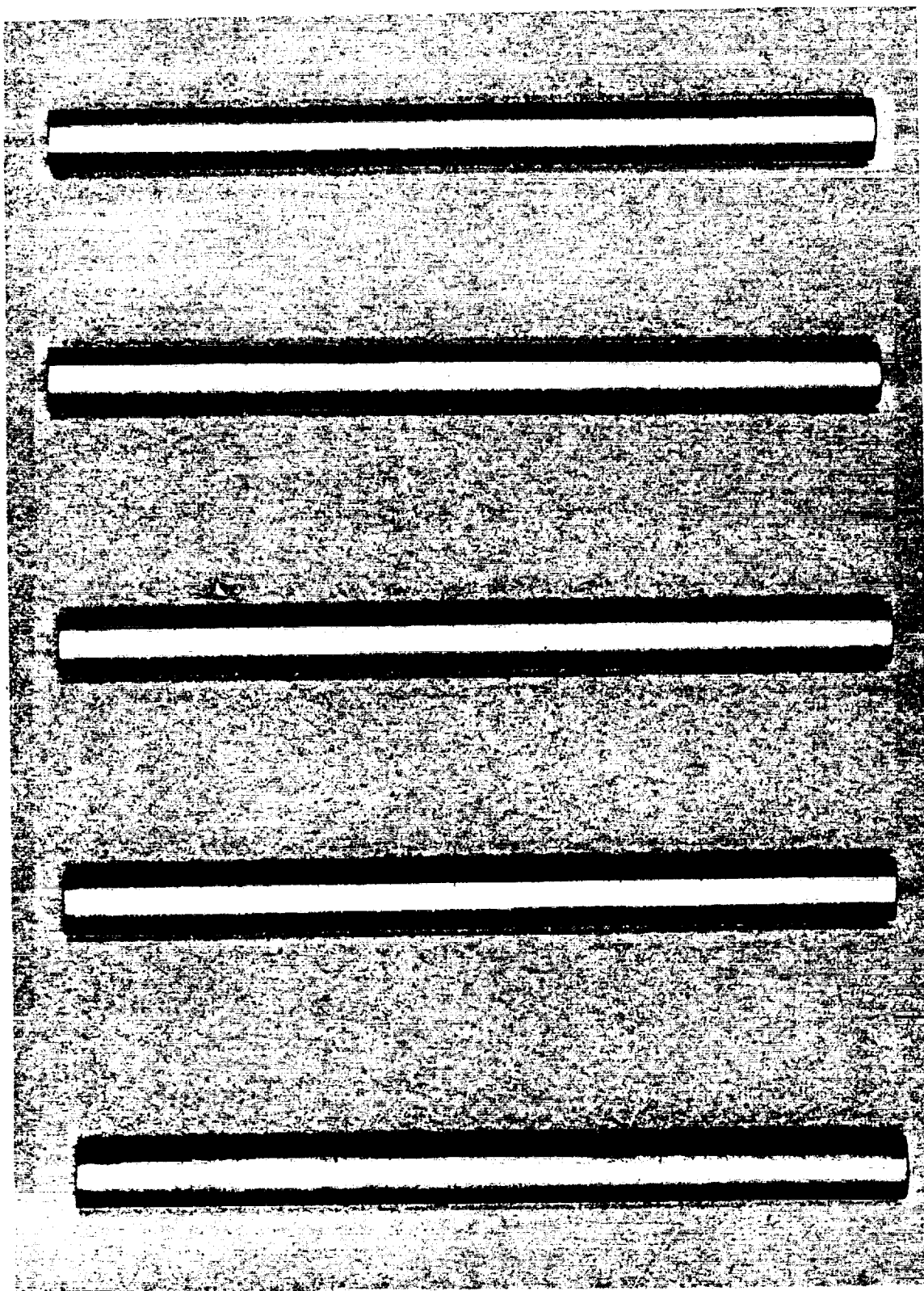


FIG. 25 APPEARANCE OF SPECIMENS AFTER STORAGE; TEST NOS. 0263 TO 0268



0274
TA-6063-99

0273

0272

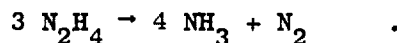
0271

0269

FIG. 26 APPEARANCE OF SPECIMENS AFTER STORAGE; TEST NOS. 0269 TO 0274

VII. DECOMPOSITION OF HYDRAZINE AND STORAGE PROBLEMS

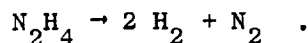
It was stated in Section IV (Hydrazine) that compatibility ratings were based on the pressure developed by the decomposition of hydrazine according to the equation:



In order to demonstrate that this is indeed the mode of decomposition, a detailed analysis of the hydrazine storage tests was conducted using all of the available data with few assumptions:

- (1) Although the initial analyses of the propellants introduced into the capsules were incomplete, and the procedures and their accuracies are not known, general familiarity with propellant-grade hydrazine makes it reasonable to assume that the initial content of NH_3 in the hydrazine introduced into test capsules is about 0.1% (Table 4).
- (2) From the measured fuel weight and the terminal analysis for ammonia in solution (Table 7), the weight of NH_3 was computed, corrected for the original content, and converted to total millimoles of NH_3 formed during storage. It was assumed that the greater part by far of the NH_3 in the capsules was contained in solution when the capsules were opened in the dry-box (see Part III). (Consideration of the data given in Table 21 suggests that even if the ammonia analysis was low by as much as 20%, the conclusions made about decomposition are not invalidated.)
- (3) Total millimoles of gas in the ullage volume were computed from measurements of the ullage volume and the terminal pressure at -196°C (Table 8). The analysis of the noncondensable gases in the ullage volume provided the ratio of nitrogen to hydrogen, and thus the total millimoles of nitrogen formed could be computed.

The results of the above computations are summarized in Table 21 as computed millimoles of NH_3 , N_2 , and H_2 and also as final molar ratios. The data in Table 21 support the premise that the decomposition of hydrazine produces essentially only ammonia and nitrogen. The presence of small amounts of hydrogen suggests that there is only a small tendency for hydrazine to decompose as follows:

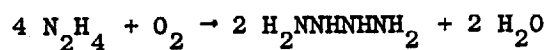


An alternative decomposition route may take place in an hydroxyl medium:

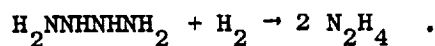


but the observed hydrogen content is so small that alternative reactions of this type must also be of minor importance.

The consumption of oxygen (refer to Part IV) may produce small amounts of water and a tetrazene:



and the tetrazene may be reduced by hydrogen:



However, the amount of oxygen present in the ullage space at the start of the test is insufficient to account for the observed increase in water content and, thus, the observed hydrogen content must be essentially that produced by minor decomposition routes.

In view of the fact that all of the test capsules had essentially the same ullage volume and the same fluid volume (within a factor of 2) and the exposed glass surfaces and gage surfaces were also identical, it is impossible to draw any conclusions about whether the hydrazine

decomposition occurred in the vapor phase or in the liquid phase; the rate of hydrazine decomposition in control samples as well as in capsules containing compatible specimens was nearly the same (about 40 mg/yr). Because of this set of circumstances, it is impossible to determine whether the observed decomposition rate of hydrazine was a function of the exposed surface area of Pyrex glass; scattered reports in the literature have indicated that decomposition is accelerated in Pyrex glass. It was also reported that decomposition could be curtailed for as much as six months if the glass were scrupulously cleaned. The pressure data for the JPL hydrazine samples indicates that decomposition was scarcely observable (~ 1 psia) for the control and compatibility tests during about the first six months of storage.

Since the glassware was cleaned according to JPL Spec. No. GMZ-50521-GEN-A, it is anticipated that the surface will have an initial coating of chromic oxide which may only in part be removed by subsequent treatment with nitric acid. More damaging, however, is the final immersion of the glass surface in concentrated ammonium hydroxide for, in this instance, extensive studies have shown that the surface layer of the glass will be hydroxylic in nature and therefore catalytic for the decomposition of hydrazine. There is severe question whether the subsequent glass-blowing operations have not introduced extraneous substances which conceivably could catalyze decomposition. Incidentally, the procedures for filling test vessels described in the above JPL Specification will permit the accumulation of water in the propellant sample, and this may be the source for both water and impurities observed in the earlier parts of this report.

The possibility of catalytic decomposition of hydrazine fuels in contact with Kovar metal and the stainless steel metal Bourdon tubes in the pressure measuring system has been given consideration. A select number of gages, and particularly those associated with test capsules having elevated pressures, were dissected and examined for indication of the presence of reactive surfaces or reaction products. Figs. 27 to 28 clearly reveal that the inner surfaces of some of the Bourdon tubes

and Kovar connections were discolored but it was not possible to correlate discoloration with increased pressure. It must be concluded that the catalytic effect of the gages and Kovar tubing must be negligible or remarkably constant.

Corrosion of the Kovar and of the Bourdon tube material would introduce nickel and cobalt into the propellant samples. The presence of cobalt in the propellant samples would be diagnostic of Kovar corrosion since this alloy contains 17% cobalt. The presence of large amounts of nickel could indicate corrosion of either the Kovar or the Bourdon tube. Accordingly, samples of the JPL propellants were analyzed for cobalt spectrophotometrically (nitroso-R) and for nickel by atomic absorption; the results are indicated in Table 22, in which there are also included values for the nickel and cobalt contents of three separate lots of hydrazine available at SRI. It is evident that nickel may be present to the extent of about 2 ppm in hydrazine but cobalt is always less than 0.2 ppm. The data in Table 22 indicate that the Kovar was not corroded and that the stainless steel Bourdon tubes also were not corroded because the nickel content was not increased appreciably.

Table 21
PRODUCTS OF HYDRAZINE DECOMPOSITION

JPL TEST NO.	MILLIMOLES OF DECOMPOSITION PRODUCTS			MOLE RATIOS OF DECOMPOSITION PRODUCTS		
	NH ₃	N ₂	H ₂	NH ₃	N ₂	H ₂
0094	5.8	1.58	0.09	3.7	1.0	0.05
0105	8.5	2.27	0.16	3.8	1.0	0.07
0107	10.3	2.55	0.05	3.7	1.0	0.02
0108	5.7	1.16	0.05	4.9	1.0	0.05
0133	4.7	1.16	0.05	4.2	1.0	0.03
0138 ^c	6.8	2.04	0.17	3.4	1.0	0.08
0155	4.0	1.05	0.05	3.8	1.0	0.05
0179 ^c	3.3	0.60	0.04	5.5	1.0	0.06
0181	10.7	2.69	0.05	4.0	1.0	0.02
0243	2.4	0.67	0.05	3.6	1.0	0.07

^c N₂H₄ control samples.

Table 22
TRACE METALS IN AMINE FUELS

SAMPLE	SPECIMEN OR IDENTIFICATION	FUEL	COBALT, ppm ^a	NICKEL ppm
JPL 0138	Control	N ₂ H ₄	0.2	0.08
JPL 0133	6061-T6 aluminum, brazed joint	N ₂ H ₄	0.2	0.06
JPL 0222	6Al-4V-2Sn titanium + 6061-T6 aluminum	N ₂ H ₄ -N ₂ H ₅ NO ₃	0.2	0.58
JPL 0241	Control	N ₂ H ₄ -N ₂ H ₅ NO ₃	0.2	0.54
JPL 0151	Control, with gage	N ₂ H ₄ -N ₂ H ₅ NO ₃	0.2	1.90
JPL 0151*	Control, all glass	N ₂ H ₄ -N ₂ H ₅ NO ₃	0.2	1.90
JPL 0269A	Control	N ₂ H ₄ -UDMH	0.2	0.16
JPL 0274	6Al-4V titanium	N ₂ H ₄ -UDMH	0.2	0.16
SRI Lot #10	n.a.	N ₂ H ₄	0.05	0.35
SRI Lot #13	n.a.	N ₂ H ₄	0.05	1.40
SRI Lot #NK	n.a.	N ₂ H ₄	0.05	0.73

^a Since only small amounts of JPL propellants were available, the accuracy of the analysis was limited to 0.2 ppm detectable; larger amounts of SRI propellant permitted lower detection limit.

NOT REPRODUCIBLE

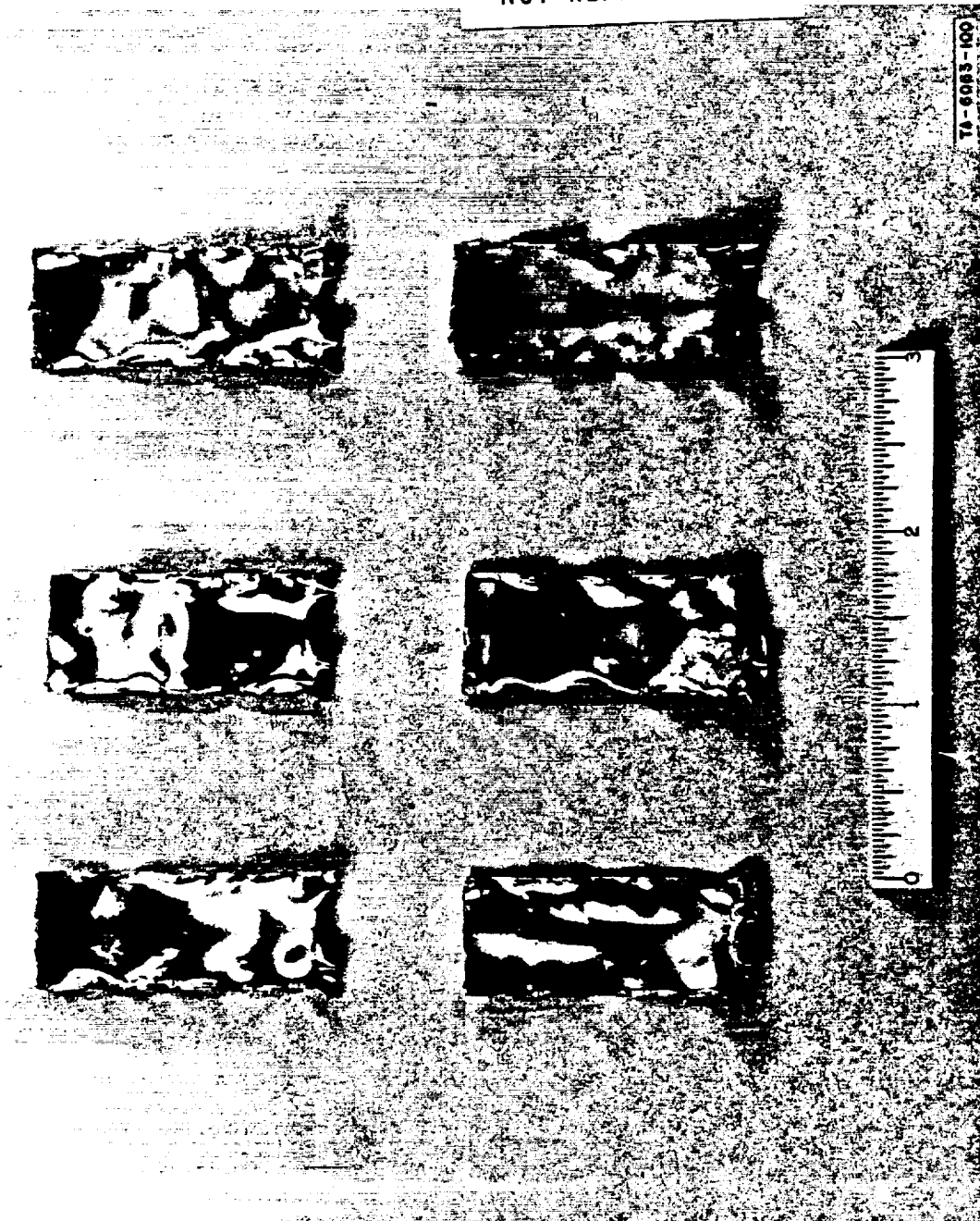


FIG. 27 INTERIOR SURFACES OF KOVAR TUBING FROM TEST NOS. 0138, 0131, 0241, 0222, 0269A, AND 0274

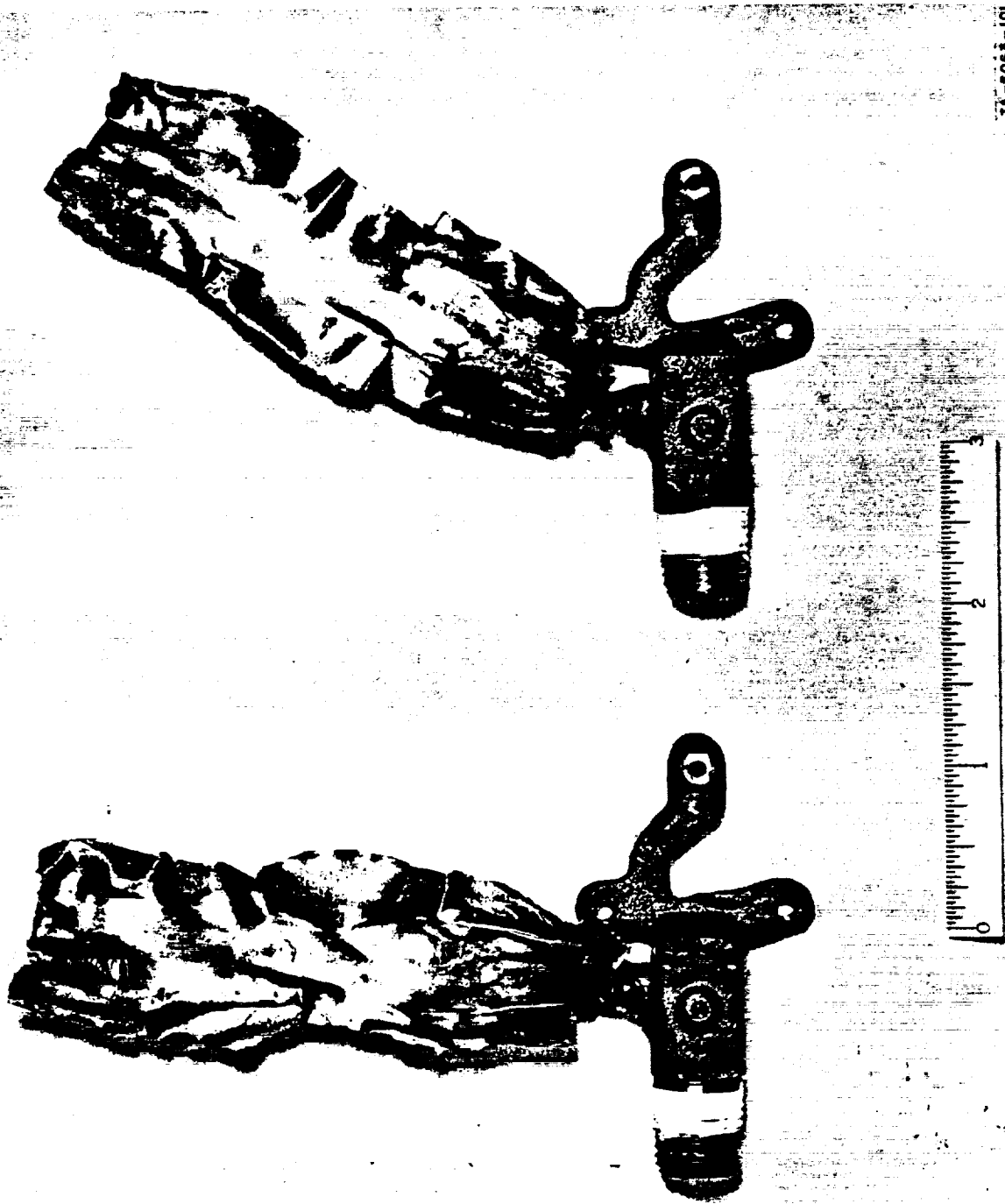


FIG. 28 INTERIOR SURFACES OF TYPICAL BOURDON GAGE TUBES FROM TEST NOS. 0138 AND 0133

APPENDIX A

CLEANING AND PASSIVATING PROCEDURES JPL SPEC NO. GMZ-50521-GEN-A

Log No. 0087 Cleaning Procedure for Metallic Specimens

<u>Step</u>	<u>Solution/Treatment</u>
1.	Vapor degrease, or degrease by immersion in acetone
2.	Air dry.

Log No. 0124 Cleaning Procedure for Elastomers

<u>Step</u>	<u>Solution/Treatment</u>	<u>Temp., °F</u>	<u>Time</u>
1.	4.0% liquid detergent in water	180 ± 30	5 minutes or more
2.	Distilled water rinse		Until pH of run-off water equals pH of source water within pH 0.5
3.	Dry by blowing off with oil-free, moisture-free nitrogen gas		

Log No. 0088 Passivating Procedure for Wrought Aluminum Alloys

<u>Step</u>	<u>Solution/Treatment</u>	<u>Temp., °F</u>	<u>Time</u>
1.	5 oz Na_3PO_4 /gal water	180-200	Until bright appearance (1-3 min)
2.	Distilled water rinse		Until pH of run-off water equals pH of source water within pH 0.5
3.	1% HF, 1% HNO_3 , 98% H_2O		1 minute
4.	same as step 2		
5.	Dry by blowing moisture off with oil-free, moisture-free nitrogen gas, or bake in vacuum oven at 120°F/5 min		

Log No. 0093 Passivating Procedure for Titanium Alloys

<u>Step</u>	<u>Solution/Treatment</u>	<u>Temp., °F</u>	<u>Time</u>
1.	HNO_3 , 1-1/2 pints/gal; HF, 3 oz/gal; H_2O , remainder	Room	1 min
2.	Distilled water rinse	Room	Until pH of run-off water equals pH of source water within pH 0.5
3.	Dry by blowing moisture off with oil-free, moisture-free nitrogen gas or bake in a vacuum oven at 120°F/5 min		

APPENDIX B
ALLOY COMPOSITIONS

<u>Alloy</u>	<u>Minor Components</u>
<u>Titanium</u>	
6Al-4V titanium	5.5-6.5 Al, 3.5-4.5 V, <0.25 Fe, <0.08 C, 0.015 H, <0.13 O, <0.05 Ni.
6Al-6V-2Sn titanium	5-6 Al, 5-6 V, 1.5-2.5 Sn, 0.35-1.0 Cu, 0.35-1.0 Fe
5Al-2.5Sn titanium	4-6 Al, 2-3 Sn
<u>Aluminum</u>	
6061-T6 aluminum	0.15-0.40 Cu, 0.4-0.8 Si, 0.8-1.2 Mg, <0.15 Ti, 0.15-0.35 Cr, <0.7 Fe, <0.15 Mn, <0.2 Zn
356-T6 aluminum	0.2 Cu, <0.6 Fe, 6.7-7.5 Si, 0.2-0.4 Mn, <0.3 Mg, <0.3 Zn, <0.2 Ti

